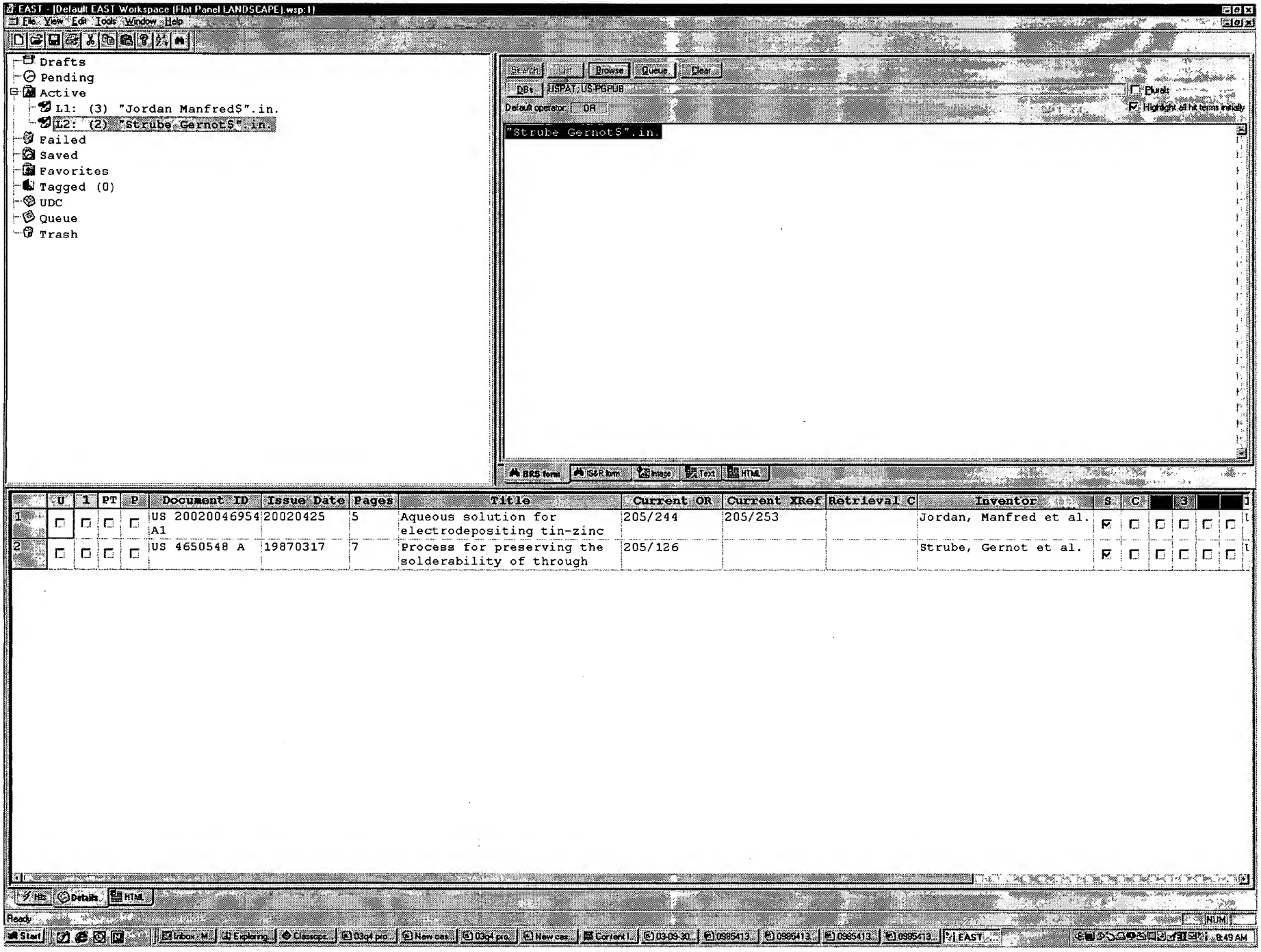
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Aqueous solution for electrodepositing tin-zinc
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17	US 4508790 A	10				☑				USPAT
18	US 4488942 A	10				☑				USPAT
19	US 4428803 A	6				☑				USPAT
20	US 4401526 A	9				☑				USPAT
21	US 4299671 A	7				☑				USPAT
22	US 4290860 A	7				☑				USPAT
23	US 4168223 A	8				☑				USPAT

US-PAT-NO: 4168223

DOCUMENT-IDENTIFIER: US 4168223 A

TITLE: Electroplating bath for depositing tin or tin alloy with brightness

---------- KWIC ---------

Abstract Text - ABTX (1):
An electroplating bath for depositing tin or a tin alloy with satisfactory brightness, which comprises a mother bath of a pH-value ranging from 4 to 8 and containing citric acid or its salt, an ammonium salt and a water-soluble polymer as a brightener. The bath may further comprise an aldehyde compound as a co-brightener.

Brief Summary Text - BSTX (1):
The present invention relates to an electroplating bath for depositing tin or a tin alloy with brightness, and more particularly to such a bath containing citric acid or its salt and an ammonium salt.

Brief Summary Text - BSTX (5):
In order to overcome the disadvantages as referred to, a bath containing citric acid or its salt and an ammonium salt has been proposed (see, for instance, USSR Inventor's Certificate No. 293,876).

Brief Summary Text - BSTX (6):
In the printed specification for said USSR Inventor's Certificate, there is a disclosure that dextrine and gelatine are added as brighteners to attain a finer and crystalline tin-zinc alloy deposition with a brightness. However, the "brightness" to be attained by this Inventor's Certificate process is of the degree "dull" or "mat" among the brightness degrees comprising bright (mirror bright), semi-bright, dull, mat and dendrite.

Brief Summary Text - BSTX (7):
In order to improve the brightness, one of the present inventors has proposed together with others a brightener for tin-zinc alloy electroplatings, which is a water-soluble polymer obtained by reacting an aliphatic amine with an organic acid ester and then further reacting the reaction product with phthalic acid anhydride, or adding to the final reaction product an aromatic aldehyde as a co-brightener (Jap. Pat. Appln. No. 148 687/1974 which was early opened under the number of 75 632/1976). The brightener is advantageous in attaining a "bright" or "semi-bright" tin-zinc alloy electroplating regardless of a kind of the metal to be plated or an electroplating bath to be employed. The brightener, however, has a practical disadvantage that the range of working current density required during the electroplating is relatively narrow.

Brief Summary Text - BSTX (9):
A specific object of the present invention is to provide an electroplating

United States Patent [19]

Igarashi et al.

[11] **4,168,223**

[45] **Sep. 18, 1979**

[54] **ELECTROPLATING BATH FOR DEPOSITING TIN OR TIN ALLOY WITH BRIGHTNESS**

[75] Inventors: Shuji Igarashi; Yoshikazu Fujisawa; Toshio Igarashi, all of Tokyo, Japan

[73] Assignee: Dipsol Chemicals Co., Ltd., Tokyo, Japan

[21] Appl. No.: 960,944

[22] Filed: Nov. 15, 1978

[30] Foreign Application Priority Data

Nov. 16, 1977 [JP] Japan 52-136730
Nov. 16, 1977 [JP] Japan 52-136731

[51] Int. Cl.² C25D 3/32; C25D 3/60

[52] U.S. Cl. ..... 204/43 S; 204/44; 204/54 R

[58] Field of Search ..... 204/43 S, 54 R, 54 L, 204/44, 120, 123; 106/1.25, 1.22

[56] References Cited

U.S. PATENT DOCUMENTS

3,616,306	10/1971	Comoby et al.	204/54 R
3,769,182	10/1973	Hsu	204/43 S
3,892,637	7/1975	Pohl	204/43 S X
3,905,878	9/1975	Dohi et al.	204/43 S

FOREIGN PATENT DOCUMENTS

1469547	4/1977	United Kingdom	204/435

Primary Examiner—G. L. Kaplan
Attorney, Agent, or Firm—Birch, Stewart, Kolasch, and Birch

[57] ABSTRACT

An electroplating bath for depositing tin or a tin alloy with satisfactory brightness, which comprises a mother bath of a pH-value ranging from 4 to 8 and containing citric acid or its salt, an ammonium salt and a water-soluble polymer as a brightener. The bath may further comprise an aldehyde compound as a co-brightener.

8 Claims, No Drawings

w/2 152 polymerization

w/4 Ex 2

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	Document ID	Pages	1	3	U	S	C	P	Kind Codes	Sou
19	US 5182006 A	9				☑				USPAT
20	US 4969980 A	17				☑				USPAT
21	US 4904544 A	7				☑				USPAT
22	US 4877494 A	36				☑				USPAT
23	US 4820388 A	5				☑				USPAT
24	US 4801368 A	10				☑				USPAT
25	US 4384930 A	10				☑				USPAT

US-PAT-NO: 4384930

DOCUMENT-IDENTIFIER: US 4384930 A

TITLE: Electroplating baths, additives therefor and methods for the electrodeposition of metals

---------- KWIC ---------

Abstract Text - ABTX (1):
Bright level metal deposits can be obtained on substrates from aqueous acid plating baths containing water soluble salts of the metal to be deposited and at least one surfactant of the formula

Brief Summary Text - BSTX (3):
The electrodeposition of metals from aqueous solutions of the metal ions is well known. The present invention is concerned particularly with aqueous acid electroplating baths for depositing metals such as tin, lead, copper, zinc, cadmium or tin-lead mixtures. The composition of the metal electroplating bath will be determined at least in part by the particular metal to be electrodeposited. Various additives have been proposed in the art for improving the effectiveness of electroplating baths containing various metals.

Brief Summary Text - BSTX (4):
In acidic electroplating baths, it is conventional to utilize a surfactant therein to control properties of the metal deposit and to assist in solubilizing other organic components. A wide variety of compositions have been suggested as surfactants in acid electroplating baths, and many of these are commercially available polyethylene oxide-based materials, and, therefore, typically contain a hydrophilic and hydrophobic portion within their chemical structure.

Brief Summary Text - BSTX (5):
The present invention is directed particularly to improved aqueous acidic plating baths for depositing tin and/or lead coatings. Generally, these plating baths contain, in addition to the water-soluble tin and/or lead salts, at least one group selected from the group consisting of fluoborates, fluosilicates, sulfates, sulfamates, etc. In addition to these basic ingredients, the prior art has suggested improvements in such baths by including additives which will improve the brightness of the deposit obtained from such baths. In U.S. Pat. No. 3,875,029, the use of a naphthalene monocarboxyaldehyde either alone or in combination with certain substituted olefins described in the patent results in an improvement in the brightness of the deposit. Other ingredients which have been suggested as being useful additives in tin and/or lead plating baths include various combinations of carbonyl-containing compounds such as aldehydes, ketones and carboxylic acids, etc. For example, U.S. Pat. No. 3,749,649 describes the advantages of utilizing tin-lead plating baths containing at least one polyether surfactant and at least one aromatic aldehyde containing a chloro substituent. Another bath for producing bright deposits of tin-lead alloys is described in U.S. Pat. No. 3,785,939.

United States Patent [19]

Eckles

[11] **4,384,930**

[45] **May 24, 1983**

[54] **ELECTROPLATING BATHS, ADDITIVES THEREFOR AND METHODS FOR THE ELECTRODEPOSITION OF METALS**

[75] Inventor: **William E. Eckles, Cleveland Heights, Ohio**

[73] Assignee: **McGean-Rohco, Inc., Cleveland, Ohio**

[21] Appl. No.: **294,976**

[22] Filed: **Aug. 21, 1981**

[51] Int. Cl.³ **C25D 3/22; C25D 3/26; C25D 3/38; C25D 3/60**

[52] U.S. Cl. ..... **204/43 S; 204/45 R; 204/50 R; 204/52 R; 204/53; 204/54 R; 204/55 R; 204/DIG 2**

[58] Field of Search ..... **564/505; 562/564; 204/45 R, 45 A, 45.5, 46 R, 46 G, 47, 48, 49, 50 R, 50 Y, 51, 52 R, 52 Y, 53, 54 R, 54 L, 55 R, 55 Y, 43 R, 43 Z, 43 G, 43 S, 43 T, 43 N, 43 P, 44, DIG. 2**

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,135,991 1/1979 Canaris et al. ..... 204/43 S
4,235,811 11/1980 Schulze et al. ..... 564/505 X

Primary Examiner—G. L. Kaplan
Attorney, Agent, or Firm—Maky, Renner, Otto & Boisselle

[57] **ABSTRACT**

Bright level metal deposits can be obtained on substrates from aqueous acid plating baths containing water soluble salts of the metal to be deposited and at least one surfactant of the formula

$$ROCH_2CH(CH_3)OCH_2CH(CH_3)N(H)CH_2CH_2COOH \quad (I)$$

or

$$ROCH_2CH(CH_3)OCH_2CH(CH_3)N\begin{matrix}(CH_2CH_2O)_xH\\(CH_2CH_2O)_yH\end{matrix} \quad (II)$$

wherein R is an alkyl group containing 10 to 12 carbon atoms; x and y are integers, the sum of which is from 2 to about 20. The aqueous acid plating baths of the invention will preferably contain as a brightening agent, at least one carbonyl-containing compound. These plating baths exhibit low foaming characteristics.

33 Claims, No Drawings

EAST Browser - L11: (45) 6 and 10 | US 4820388 A | Tag: S | Doc: 23/45 (SORTED) | Format: KWIC

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18	US 5525207 A	5											☑				USPAT
19	US 5182006 A	9											☑				USPAT
20	US 4969980 A	17											☑				USPAT
21	US 4904544 A	7											☑				USPAT
22	US 4877494 A	36											☑				USPAT
23	US 4820388 A	5											☑				USPAT

US-PAT-NO: 4820388

DOCUMENT-IDENTIFIER: US 4820388 A

TITLE: Polyalkylene glycol naphthyl-3-sulfopropyl diether compounds and their salts, process for preparing same and electroplating baths containing same

---------- KWIC ---------

Abstract Text - ABTX (1):
Novel Polyalkylenglycol naphthyl-3-sulfopropyl diethers and salts thereof of the formula ##STR1## (R.sub.1 -R.sub.3 =H, C.sub.p H.sub.2p--1 ; p=1--4, A=(PO).sub.m --(EO).sub.n --, (EO).sub.n --(PO).sub.m,--(EO).sub.n EO=ethylenoxide residue, PO=propylenoxide residue, m=0-15, n-1-40, A=H, alkali metal, earth alkali metal, NR.sub.5 R.sub.6 R.sub.7 R.sub.8 wherein R.sub.5 -R.sub.8 =H, C.sub.1 -C.sub.4 --alkyl, aryl, aralkyl) are prepared by reacting the corresponding polyalkylene glycol naphthyl either with propane-1.3-sultone. The compounds are surfactants in particular in electroplating baths for precipitation Zn, Sn, Cu, Ag, Ni and alloys thereof.

Brief Summary Text - BSTX (1):
The invention relates to novel Polyalkylene glycol naphthyl-3-sulfopropyl diethers and salts thereof as well as a process for preparing these compounds and electroplating baths containing these compounds as surfactants.

Brief Summary Text - BSTX (2):
It is known to use ethoxylated .beta.-naphthol as surfactant when depositing metals from electroplating baths. These compounds are in particular suited to keep the chemical brightenners in solution and to act as wetting agents for the cathode surface and to prevent the formation of the so-called hydrogen pores which occur when hydrogen is fixed at the cathodic metal surface together with the metal to be deposited such as zinc, cadmium, copper, silver and the like. However, the solubility of these non-ionic compounds is strongly dependant from pH, from the salt concentration, from the temperature and from the chain length of the molecules. The compounds are not suited for high perfomance electroplating baths which are used at high current densities up to about 150 A/dm.sup.2 and increased temperature up to about 79.degree. C.

Brief Summary Text - BSTX (10):
The use of the compounds of the invention as surfactant in electroplating baths is also possible with compounds having m=0. Particularly preferred are compounds wherein m=1 to 5 and n=2 to 24, in particular 6 to 10. Useful for the galvanotechnic purposes are not only derivatives of .alpha.- and .beta.-naphtol but also substituted derivatives thereof wherein 1 to 3 substituents which may be equal or different, in particular methyl, ethyl, propyl, isopropyl, butyl and isobutyl may be present. The presence of such substituents is not disadvantageous for the stability of such compounds.

Brief Summary Text - BSTX (13):
The amounts of the compounds of the invention to be used in electroplating

United States Patent [19]

Kurze et al.

[11] **Patent Number: 4,820,388**

[45] **Date of Patent: Apr. 11, 1989**

[54] **POLYALKYLENE GLYCOL NAPHTHYL-3-SULFOPROPYL DIETHER COMPOUNDS AND THEIR SALTS, PROCESS FOR PREPARING SAME AND ELECTROPLATING BATHS CONTAINING SAME**

[75] Inventors: **Werner Kurze, Neuhofen; Klaus-Peter Klos, Trebur, both of Fed. Rep. of Germany**

[73] Assignees: **Raschig AG, Ludwigshafen; Elektro-Brite GmbH & Co. KG, Trebur, both of Fed. Rep. of Germany; a part interest**

[21] Appl. No.: **205,631**

[22] Filed: **Jun. 13, 1988**

[30] **Foreign Application Priority Data**

Jul. 9, 1987 [DE] Fed. Rep. of Germany 3722778

[51] Int. Cl.[4] C07C 143/30; C07C 143/32; C07C 143/34

[52] U.S. Cl. ..... 204/44.2; 106/1.25; 204/43.1; 204/44; 204/44.4; 204/44.5; 204/45.1; 204/46.1; 204/49; 204/52.1; 204/54.1; 204/55.1; 260/512 C

[58] Field of Search ..... 260/512 C; 204/43.1, 204/44.2, 44.3, 44.4, 44.5, 44.6, 44.7, 44, 45.1, 45.5, 46.1, 47, 47.5, 48, 49, 50.1, 50.3, 51, 52.1, 52.5, 53, 54.1, 54.5, 55.1, 55.3, 55.5; 106/1.25

[56] **References Cited**

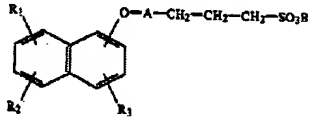
U.S. PATENT DOCUMENTS

4,153,575 5/1979 Kalfoglou et al. ..... 260/512 CX

Primary Examiner—G. L. Kaplan
Attorney, Agent, or Firm—Collard, Roe & Galgano

[57] **ABSTRACT**

Novel Polyalkylenglycol naphthyl-3-sulfopropyl diethers and salts thereof of the formula



(R_1–R_3=H, C_pH_{2p-1}; p=1—4, A=$(PO)_m$—$(EO)_n$—, $(EO)_n$—$(PO)_m$—$(EO)_n$ EO=ethylenoxide residue, PO=propylenoxide residue, m=0—15, n—1—40, A=H, alkali metal, earth alkali metal, $NR_5R_6R_7R_8$ wherein R_5–R_8=H, C_1–C_4—alkyl, aryl, aralkyl) are prepared by reacting the corresponding polyalkylene glycol naphthyl either with propane-1.3-sultone. The compounds are surfactants in particular in electroplating baths for precipitation Zn, Sn, Cu, Ag, Ni and alloys thereof.

7 Claims, No Drawings

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	Document ID	Pages	1	3	U	S	C	P	Kind Codes	Sou
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33	US 20030150743 A	12				☑				US-PG
34	US 20030141192 A	14				☑				US-PG
35	US 20030070933 A	5				☑				US-PG
36	US 20030066756 A	12				☑				US-PG
37	US 20020187364 A	6				☑				US-PG
38	US 20020187355 A	8				☑				US-PG

[0008] Certain polyalkyleneimines are known for use in zinc electroplating baths. See, for example, German Patent Application DE 3121016. Such polyalkyleneimines may be substituted with carbamoyl and/or thiocarbamoyl groups. The use of polyalkyleneimines is not disclosed for use in tin or tin-alloy plating baths.

[0009] U.S. Pat. No. 5,282,954 (Opaskar) discloses alkoxylated diamine surfactants for use in tin electroplating baths. Carboxyalkylated polyalkyleneimines are not disclosed in this patent.

[0010] There is a continuing need for plating baths that will deposit tin or tin-alloys over a wide current density range while maintaining a uniform deposit appearance over the current density range, particularly for use in high speed plating systems.

SUMMARY OF THE INVENTION

[0011] It has been surprisingly found that tin or tin-alloy may be uniformly deposited over a wide current density range using the electrolyte compositions of the present invention. It has been further surprisingly found that the electrolyte compositions of the present invention plate tin or tin-alloy at high current densities with low metal concentrations, while producing a uniform deposit appearance over the entire current density range.

[0012] In one aspect, the present invention provides an electrolyte composition for depositing tin or tin-alloy on a substrate, including one or more tin compounds, one or more acidic electrolytes, and one or more carboxyalkylated polyalkyleneimine compounds.

[0013] In another aspect, the present invention provides a method for depositing tin or tin-alloy on a substrate including the steps of contacting the substrate with the electrolyte composition described above and applying a sufficient current density to the electrolyte composition to deposit the tin or tin-alloy on the substrate.

[0014] In yet another aspect, the present invention provides a substrate having a tin or tin-alloy deposited thereon according to the method described above.

[0015] In a further aspect, the present invention provides an electrolyte composition for depositing tin-copper alloy on a substrate, including one or more tin compounds, one or more copper compounds, one or more acidic electrolytes, and one or more carboxyalkylated polyalkyleneimine compounds.

[0016] In a still further aspect, the present invention provides a method for high speed electroplating of tin or tin-alloys including the steps of: a) utilizing high speed electroplating equipment comprising an electroplating cell; an overflow reservoir adjacent the cell; means for returning solution from the reservoir to the electroplating cell; means for directing a substrate to be plated from an entry point at one end of the cell to an exit at a second end of the cell; b) introducing an electrolyte including a basis solution of one or more tin compounds, one or more acidic electrolytes, and one or more carboxyalkylated polyalkyleneimine compounds; and c) continuously electroplating substrates with tin or tin-alloy at a sufficient current density and at a sufficient temperature for high speed electroplating as the substrates pass through the electroplating solution within the cell.

[0017] In yet a further aspect, the present invention provides a method of

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2002/0187355 A1**

Crosby (43) **Pub. Date: Dec. 12, 2002**

(54) **TIN PLATING**

(75) Inventor: **Jeffrey N. Crosby**, Warwickshire (GB)

Correspondence Address:
S. Matthew Cairns
c/o EDWARDS & ANGELL, LLP
Dike, Bronstein, Roberts & Cushman, IP Group
P.O. Box 9169
Boston, MA 02209 (US)

(73) Assignee: **Shipley Company, L.L.C.**, Marlborough, MA

(21) Appl. No.: **10/139,562**

(22) Filed: **May 6, 2002**

(30) **Foreign Application Priority Data**

May 24, 2001 (GB) 0112599.6
May 25, 2001 (GB) 0112769.5

Publication Classification

(51) Int. Cl.[7] C25D 3/60; B32B 15/00
(52) U.S. Cl. 428/432; 205/252; 205/300

(57) **ABSTRACT**

Electrolyte compositions for the deposition of tin and tin-alloys on a substrate are disclosed, along with methods of electroplating tin and tin-alloys using such compositions. These electrolyte compositions are useful for high speed tin plating.

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36	US 20030066756 A	12					☑				US-PG
37	US 20020187364 A	6					☑				US-PG
38	US 20020187355 A	8					☑				US-PG
39	US 20020170828 A	5					☑				US-PG
40	US 20020153260 A	8					☑				US-PG
41	US 20020104763 A	11					☑				US-PG

[0034] The content of thioamide compound or thiol compound in the plating bath should preferably be 1-200 g/L, particularly 5-100 g/L. They will not fully produce their effect if their amount is excessively small; they will prevent the formation of fine crystals in the plating film if their amount is excessively large.

[0035] The plating bath of the present invention may be incorporated with a nonionic surface active agent if necessary.

[0036] A nonionic surface active agent helps the Sn--Cu alloy deposition with a smooth dense surface and with a uniform composition. It should preferably be one which is derived from alkylene oxide. It includes, for example, polyoxyethylene .beta.-naphthol ether, ethylene oxide-propylene oxide block copolymer, polyoxyethylene alkyl ether, polyoxyethylene phenyl ether, polyoxyethylene alkylamino ether, polyoxyethylene fatty acid ester, polyoxyethylene polyhydric alcohol ether, and polyethylene glycol. Its amount in the plating bath should preferably be 0.01-50 g/L, particularly 2-10 g/L. It may cause burnt deposits due to high current density if its amount is excessively small, and it may cause the plating film to assume a blackish color or uneven color if its amount is excessively large.

[0037] The plating bath of the present invention may be incorporated with one or more of cationic surface active agents, anionic surface active agents, and amphoteric surface active agents, if necessary.

[0038] Examples of the cationic surface active agents include dodecyltrimethyl ammonium salt, hexadecyltrimethyl ammonium salt, octadecyltrimethyl ammonium salt, dodecyldimethylethyl ammonium salt, octadecenyldimethylethyl ammonium salt, dodecyldimethyl ammonium betaine, octadecyldimethyl ammonium betaine, dimethylbenzyldodecyl ammonium salt, hexadecyldimethylbenzyl ammonium salt, octadecyldimethylbenzyl ammonium salt, trimethylbenzyl ammonium salt, triethylbenzyl ammonium salt, hexadecyl pyridinium salt, dodecyl pyridinium salt, dodecyl picolinium salt, dodecyl imidazolium salt, oleyl imidazolium salt, octadecylamine acetate, and dodecylamine acetate.

[0039] Examples of the anionic surface active agents include alkyl sulfate, polyoxyethylene alkyl ether sulfate, polyoxyethylene-alkylphenyl ether sulfate, alkylbenzenesulfonate, and (poly)alkylnaphthalenesulfonate- . Examples of the alkyl sulfonate include sodium dedecylsulfate and sodium oleyl sulfate. Examples of the polyoxyethylene alkyl ether sulfate include sodium polyoxyethylene (EO12) nonyl ether sulfate and sodium polyoxyethylene (EO15) dodecyl ether sulfate.

[0040] Examples of the amphoteric surface active agents include betaine, sulfobetaine, and imidazolium betaine. Additional examples include sulfated adduct or sulfonated adduct of a condensation product of ethylene oxide and/or propylene oxide with alkylamine or diamine.

[0041] The amount of these surface active agents in the plating bath should preferably be 0-50 g/L, preferably 0.01-50 g/L, particularly 2-10 g/L.

[0042] The plating bath of the present invention may be incorporated with one or more of mercapto group-containing aromatic compounds, dioxyaromatic compounds, and unsaturated carboxylic acid compounds, as a leveling agent for the plating film and an antioxidant for Sn.sup.2+ion in the plating bath. Examples of the mercapto group-containing aromatic compounds include 2-mercaptobenzoic acid, mercaptophenol, 2-mercaptobenzoxazole,

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2002/0104763 A1**

YANADA et al. (43) **Pub. Date: Aug. 8, 2002**

(54) **TIN - COPPER ALLOY ELECTROPLATING BATH AND PLATING PROCESS THEREWITH**

(76) Inventors: **ISAMU YANADA**, HIRAKATA-SHI (JP); **MASANOBU TSUJIMOTO**, HIRAKATA-SHI (JP); **TETSUROU OKADA**, HIRAKATA-SHI (JP); **TERUYA OKA**, HIRAKATA-SHI (JP); **HIDEYUKI TSUBOKURA**, HIRAKATA-SHI (JP)

Correspondence Address:
SUGHRUE MION ZINN MACPEAK & SEAS
2100 PENNSYLVANIA AVENUE NW
WASHINGTON, DC 200373202

(*) Notice: This is a publication of a continued prosecution application (CPA) filed under 37 CFR 1.53(d).

(21) Appl. No.: **09/433,887**

(22) Filed: **Nov. 4, 1999**

(30) **Foreign Application Priority Data**

Nov. 5, 1998 (JP) 10-314210
May 7, 1999 (JP) 11-127648

Publication Classification

(51) Int. Cl.[7] C25D 3/58; C25D 3/60
(52) U.S. Cl. 205/241; 205/253; 205/254

(57) **ABSTRACT**

A tin-copper alloy electroplating bath which comprises a water-soluble tin salt, a water-soluble copper salt, an inorganic or organic acid or a water-soluble salt thereof, and one or more compounds selected from thioamide compounds and thiol compounds. The present invention makes it possible to form a tin-copper alloy deposit, in place of tin-lead alloy plating, on electronic parts such as chips, quartz crystal oscillators, hoops, connector pins, lead frames, bumps, lead pins of packages, and printed circuit boards.

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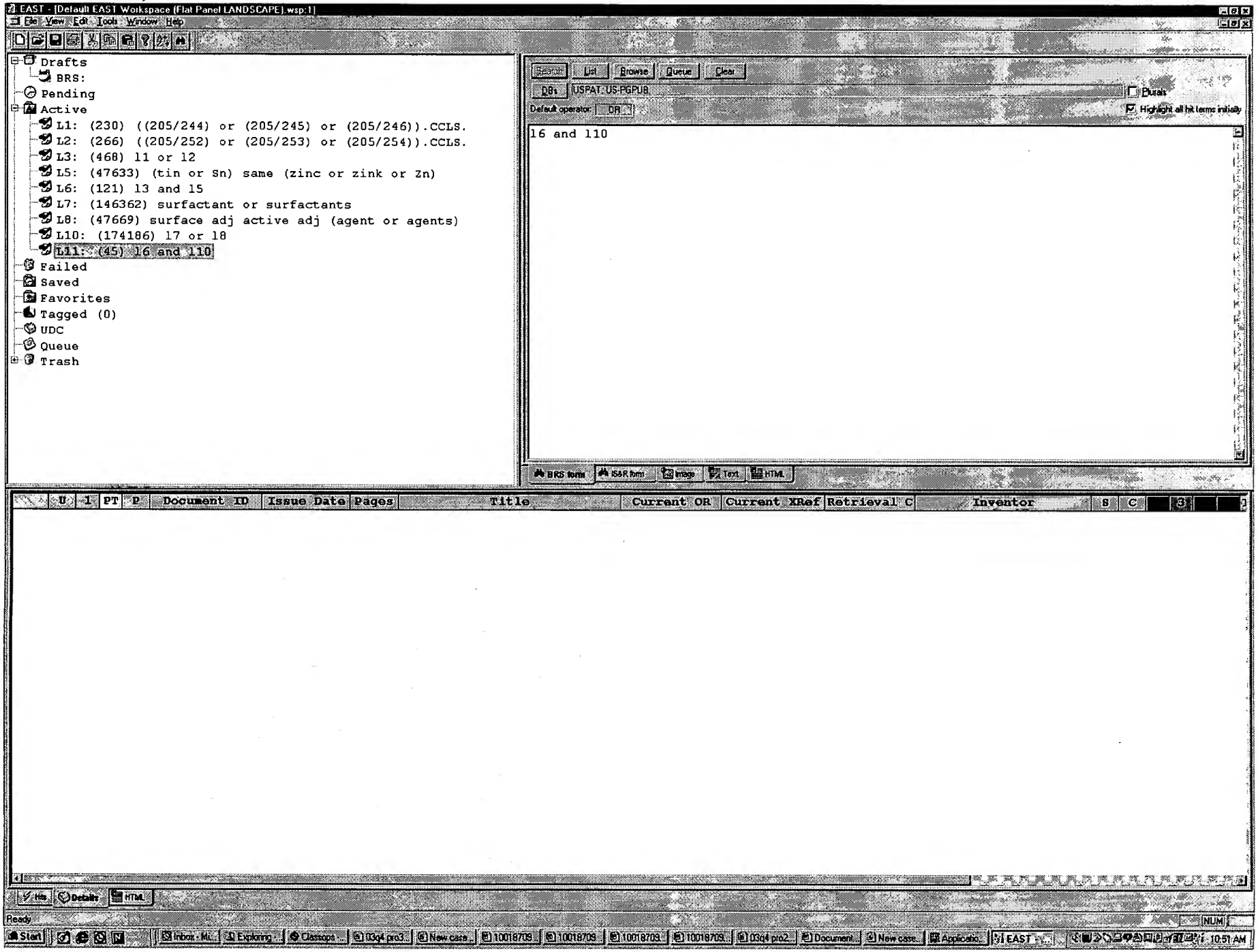
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L2: (266) ((205/252) or (205/253) or (205/254)).CCLS.
L3: (468) l1 or l2
L5: (47633) (tin or Sn) same (zinc or zink or Zn)
L6: (121) l3 and l5
L7: (146362) surfactant or surfactants
L8: (47669) surface adj active adj (agent or agents)
L10: (174186) l7 or l8
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4	US 6562220 B2	5			☑					USPAT
5	US 6508927 B2	11			☑					USPAT
6	US 6500886 B1	13			☑					USPAT
7	US 6478944 B1	13			☑					USPAT

bath upon make-up with a soluble source of zinc ions such as zinc sulfate or zinc chloride. Stannous sulfate and zinc sulfate are preferred sources of tin and zinc ions respectively. Preferably, if present, the concentration of tin ions in the electroplating bath range from about 30 to 50 g/l, most preferably from about 35 to 45 g/l. Preferably, if present, the concentration of zinc ions in the electroplating bath range from about 15 to 40 g/l, most preferably from about 20 to 35 g/l. As noted the electroplating composition is particularly effective in plating tin-zinc alloys. In this case, the electroplating bath comprises both tin and zinc ions and the concentration of tin ions preferably ranges from about 30 to 40 g/l while the concentration of zinc ions ranges from about 20 to 40 g/l.

Brief Summary Text - BSTX (22):

Other known leveling agents and co-brighteners may optionally also be added to the electroplating bath. These additional optional additives include polyethylene glycols, water soluble polypropylene oxide polymers, water soluble polyethylene oxide polymers, bis-phenol ethoxylates, alcohol ethoxylates, aromatic ethoxylates, ethoxylated fatty acids, ethoxylated amines, polyglycerines, and various surfactants. Many of the foregoing compounds are useful in providing leveling effects and in otherwise brightening the electroplated deposits. The specific compound to be selected depends upon the specific electroplating bath but the inventor has found the following compounds to be particularly useful in tin, zinc, or tin-zinc electroplating baths: diglycidyl polyethylene glycol, polyglycerine and bis-phenol ethoxylates. In general, if used, the concentration of these leveling agents and co-brighteners may range from about 0.5 to 5 g/l in the electroplating bath.

Brief Summary Text - BSTX (25):

As noted, the electroplating bath of this invention is particularly suited to plating tin-zinc alloy electrodeposits. Electrodeposits of approximately 75% tin and 25% zinc are widely used in industry in improving the corrosion resistance of steel substrates. An elemplary formulation for producing 75/25 tin-zinc electrodeposits is as follows:

Brief Summary Text - BSTX (26):

The inventor has found that the foregoing formulation is capable of delivering a 75/25 tin-zinc alloy (.+-.5%) electrodeposit over a plating current density range of 50 to 300 amps per square foot (ASF) with bright, smooth electrodeposits over steel substrates. In this case the cathode would be a steel substrate and the anode would consist of a combination of tin and zinc substrates.

Brief Summary Paragraph Table - BSTL (1):

Component Concentration Stannous Sulfate 30-50 g/l (as tin) Zinc Sulfate 20-40 g/l (as zinc) Citric Acid 25-150 g/l Ammonium Sulfate 50-150 g/l propanedioic acid diethyl ester polymer 0.5-1.5 g/l with N-(3-aminopropyl)1,3-propanediamine N-(2-carboxybenzoyl) Diglycidyl Polyethylene Glycol 0.5-1.5 g/l Polyglycerine 0.5-1.5 g/l Veratryl aldehyde 0.05-0.5 g/l

Detailed Description Text - DETX (2):

The following tin-zinc electroplating bath was formulated:

(12) **United States Patent**
Becking

(10) **Patent No.: US 6,582,582 B2**
(45) **Date of Patent: Jun. 24, 2003**

(54) **ELECTROPLATING COMPOSITION AND PROCESS**

(76) Inventor: **Donald Becking**, 138 Tanglewood Dr., Southington, CT (US) 06489

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 174 days.

(21) Appl. No.: **09/803,631**

(22) Filed: **Mar. 9, 2001**

(65) **Prior Publication Data**

US 2002/0170828 A1 Nov. 21, 2002

(51) **Int. Cl.**[7] **C25D 3/56**

(52) **U.S. Cl.** **205/244**; 205/240; 205/241; 205/252; 205/253; 205/254; 205/300; 205/301; 205/302; 205/303; 205/304; 205/305; 205/238; 205/261; 106/1.25; 106/1.16; 106/1.29; 106/1.05

(58) **Field of Search** 106/1.25, 1.16, 106/1.29, 1.05; 205/240, 241, 244, 252, 253, 254, 300, 301, 302, 303, 304, 305–314, 238, 261

(56) **References Cited**

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Primary Examiner—Roy King
Assistant Examiner—Wesley A. Nicolas
(74) *Attorney, Agent, or Firm*—Carmody & Torrance LLP

(57) **ABSTRACT**

An electroplating bath is disclosed that is particularly suited to the electrodeposition of tin, zinc and alloys of the foregoing in a smooth and bright electrodeposit. The disclosed electroplating bath comprises propanedioic acid, diethyl ester, polymer with N-(3-aminopropyl)-1,3-propanediamine, N-(2-carboxy benzoyl) as a brightener additive. In addition, the electroplating bath may also comprise carboxylic acids, ammonium salts, aldehyde compounds and a variety of co-brighteners.

32 Claims, No Drawings

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4	US 6562220 B2	5			☑					USPAT
5	US 6508927 B2	11			☑					USPAT
6	US 6500886 B1	13			☑					USPAT
7	US 6478944 B1	13			☑					USPAT

US-PAT-NO: 6562221

DOCUMENT-IDENTIFIER: US 6562221 B2

TITLE: Process and composition for high speed plating of tin and tin alloys

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Brief Summary Text - BSTX (19):

The plating composition may be used to plate tin or tin alloys. If tin alloy plating is desired then the plating composition should also comprise a source of metal ions corresponding to the alloying element(s). Suitable alloying elements include zinc, lead, copper, bismuth and nickel. If alloy plating is desired soluble sources of the foregoing metals such as nickel sulfate, copper sulfate, zinc sulfate, bismuth sulfate and lead methane sulfonate, may be employed. The concentration of the alloying element in the plating composition will range depending upon the alloy content desired in the plated deposit but is preferably from about 0.5 to 50 g/l.

Brief Summary Text - BSTX (21):

The plating composition may also preferably comprise known plating performance additives such as those described in U.S. Pat. No. 6,217,738, the teachings of which are incorporated by reference herein in their entirety. As disclosed therein these plating performance additives may include certain mono-, di-or tri-substituted phenols. These substituted phenols may have at least one substituent containing at least one secondary, tertiary, or quaternary nitrogen atom, and are said to improve the appearance and physical properties of the plate and the overall plating performance of the process. In addition to the substituted phenols or in replacement thereof, surfactants and/or water soluble polymers may also be employed as plating performance additives. Preferably the concentration of plating performance additives in the plating composition will range from about 0.5 to 20 g/l.

Current US Original Classification - CCOR (1):

205/254

(12) **United States Patent**
Crotty

(10) **Patent No.: US 6,562,221 B2**
(45) **Date of Patent: May 13, 2003**

(54) **PROCESS AND COMPOSITION FOR HIGH SPEED PLATING OF TIN AND TIN ALLOYS**

(76) Inventor: **David Crotty**, 31 Woodside Park Blvd., Pleasant Ridge, MI (US) 48069

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/965,743**

(22) Filed: **Sep. 28, 2001**

(65) **Prior Publication Data**

US 2003/0070933 A1 Apr. 17, 2003

(51) **Int. Cl.**[7] **C25D 3/32**

(52) **U.S. Cl.** **205/254**; 205/140; 205/302; 205/303

(58) **Field of Search** 205/140, 154, 205/253, 254, 301, 302, 303, 304; 106/1.22, 1.25

(56) **References Cited**

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Primary Examiner—Roy King
Assistant Examiner—William T. Leader
(74) *Attorney, Agent, or Firm*—Carmody & Torrance LLP

(57) **ABSTRACT**

A composition and process for electroplating tin or tin alloys onto a substrate at relatively high current densities. The electrolyte comprises toluene sulfonic acid and a source of ammonium ions and/or magnesium ions. The process is particularly suited to high speed reel to reel or strip steel plating.

12 Claims, No Drawings

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5	US 6508927 B2	11								USPAT
6	US 6500886 B1	13								USPAT
7	US 6478944 B1	13								USPAT

US-PAT-NO: 6562220

DOCUMENT-IDENTIFIER: US 6562220 B2

TITLE: Metal alloy sulfate electroplating baths

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Abstract Text - ABTX (1):
The use of alkali metal, alkaline earth metal, ammonium and substituted ammonium salts of alkyl and alkanol sulfonic acids as additives in pure metal and metal alloy sulfate electroplating baths has a number of unexpected benefits including wider useful current density range, improved appearance and in the case of tin improved oxidative stability. The metals and alloys include but are not limited to tin, nickel, copper, chromium, cadmium, iron, rhodium, ruthenium, iron/zinc and tin/zinc.

Brief Summary Text - BSTX (8):
It is therefore worthwhile to identify other additives that can improve the performance of metal sulfate electroplating baths. There are many examples in the prior art where surfactants and other organic additives are used to provide a more desirable finish. In the case of tin the prior art also describes additives which can improve the oxidative stability of the tin and therefore provide a bath with less sludge formation. It is less common to find examples of additives which improve the plating range especially at the high current density end. Increasing the current density is a very desirable feature but it has been difficult to identify additives which can do this without creating other problems in the bath.

Brief Summary Text - BSTX (14):
The baths that can be improved by the present invention include tin and tin alloys, nickel and nickel alloys, copper and copper alloys, chromium and chromium alloys, cadmium and cadmium alloys, iron and iron alloys, rhodium and rhodium alloys, ruthenium and ruthenium alloys, and especially the iron/zinc and tin/zinc alloy plating baths.

Brief Summary Text - BSTX (20):
These baths also contain the corresponding metal salt or metal salts if any alloy plate is required, and various additives to control the quality and appearance of the plated surface and the stability of the bath solution. Typical additives include a surfactant such as an ethoxylated fatty alcohol, a brightening agent if required and an antioxidant such as hydroquinone or catechol, if tin is one of the metals being plated.

Detailed Description Paragraph Table - DETL (1):
Bath Composition: 5% Sulfuric Acid 20.0 g/l Sn (as stannous sulfate) 3 g/l JWL 5000 surfactant 0.1 g/l salicylic acid Bath base 5 ppm 2.9 - Dimethyl - phenanthroline Run # Additive and Level Results of Plating Tests 1 No additive Dark burn on high current density edge at 5 Amps. Burn is 12 mm wide at high current density edge at 10 Amps. 2 10 g/l Sodium isethionate Even light gray satin deposit at (calculated as isethionic acid) 10 Amps - no burn.

(12) **United States Patent**
Gillman et al.

(10) **Patent No.: US 6,562,220 B2**
(45) **Date of Patent: *May 13, 2003**

(54) **METAL ALLOY SULFATE ELECTROPLATING BATHS**

(75) Inventors: **Hyman D. Gillman**, Spring City, PA (US); **Brenda Fernandes**, Cranston, RI (US); **Kazimierz Wikiel**, Wakefield, RI (US)

(73) Assignee: **Technic, Inc.**, Cranston, RI (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 74 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **09/862,166**

(22) Filed: **May 21, 2001**

(65) **Prior Publication Data**

US 2002/0014414 A1 Feb. 7, 2002

Related U.S. Application Data

(63) Continuation-in-part of application No. 09/272,800, filed on Mar. 19, 1999, now Pat. No. 6,251,253.

(51) **Int. Cl.**[7] **C25D 3/02**

(52) **U.S. Cl.** **205/239**; 205/240; 205/241; 205/244; 205/245; 205/246; 205/254; 205/255; 205/274; 205/281; 205/296; 205/302; 205/311; 205/242; 106/1.21; 106/1.25

(58) **Field of Search** 205/239, 240, 205/241, 246, 254, 255, 274, 281, 296, 302, 311, 242; 106/1.21, 1.25

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Primary Examiner—Kishor Mayekar
(74) *Attorney, Agent, or Firm*—Ernest V. Linek; Banner & Witcoff, Ltd.

(57) **ABSTRACT**

The use of alkali metal, alkaline earth metal, ammonium and substituted ammonium salts of alkyl and alkanol sulfonic acids as additives in pure metal and metal alloy sulfate electroplating baths has a number of unexpected benefits including wider useful current density range, improved appearance and in the case of tin improved oxidative stability. The metals and alloys include but are not limited to tin, nickel, copper, chromium, cadmium, iron, rhodium, ruthenium, iron/zinc and tin/zinc.

31 Claims, No Drawings

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5	US 6508927 B2	11								USPAT
6	US 6500886 B1	13								USPAT
7	US 6478944 B1	13								USPAT

Brief Summary Text - BSTX (40):
The plating bath of the present invention may be incorporated with one or more of cationic surface active agents, anionic surface active agents, and amphoteric surface active agents, if necessary.

Brief Summary Text - BSTX (41):
Examples of the cationic surface active agents include dodecyltrimethyl ammonium salt, hexadecyltrimethyl ammonium salt, octadecyltrimethyl ammonium salt, dodecyldimethylethyl ammonium salt, octadecenyldimethylethyl ammonium salt, dodecyldimethyl ammonium betaine, octadecyldimethyl ammonium betaine, dimethylbenzyldodecyl ammonium salt, hexadecyldimethylbenzyl ammonium salt, octadecyldimethylbenzyl ammonium salt, trimethylbenzyl ammonium salt, triethylbenzyl ammonium salt, hexadecyl pyridinium salt, dodecyl pyridinium salt, dodecyl picolinium salt, dodecyl imidazolium salt, oleyl imidazolium salt, octadecylamine acetate, and dodecylamine acetate.

Brief Summary Text - BSTX (42):
Examples of the anionic surface active agents include alkyl sulfate, polyoxyethylene alkyl ether sulfate, polyoxyethylene alkylphenyl ether sulfate, alkylbenzenesulfonate, and (poly)alkylnaphthalenesulfonate. Examples of the alkyl sulfonate include sodium dedecylsulfate and sodium oleyl sulfate. Examples of the polyoxyethylene alkyl ether sulfate include sodium polyoxyethylene (EO12) nonyl ether sulfate and sodium polyoxyethylene (EO15) dodecyl ether sulfate.

Brief Summary Text - BSTX (43):
Examples of the amphoteric surface active agents include betaine, sulfobetaine, and imidazolium betaine. Additional examples include sulfated adduct or sulfonated adduct of a condensation product of ethylene oxide and/or propylene oxide with alkylamine or diamine.

Brief Summary Text - BSTX (44):
The amount of these surface active agents in the plating bath should preferably be 0-50 g/L, preferably 0.01-50 g/L, particularly 2-10 g/L.

Brief Summary Text - BSTX (47):
The plating bath of the present invention may preferably be incorporated with one or more of water-soluble metal salts selected from water-soluble gold salts, water-soluble silver salts, water-soluble zinc salts, water-soluble bismus salts, water-soluble nickel salts, water-soluble cobalt salts, and water-soluble palladium salts. The incorporation of the water-soluble metal salt can form a dense ternary alloy of Sn--Cu--Au, Ag, Zn, Bi, Ni, Co or Pd due to the codeposition of the metal (Au, Ag, Zn, Bi, Ni, Co or Pd) with Sn and Cu, or the water-soluble metal salt can act as an additive for forming a dense deposit, improving a solderability, and preventing the deposit from discoloring after heat treatment.

Brief Summary Text - BSTX (52):
The plating bath of the present invention may be applied to rack plating, barrel plating, or high-speed plating in the usual way. The cathode current

(12) **United States Patent**
Yanada et al.

(10) **Patent No.: US 6,508,927 B2**
(45) **Date of Patent: *Jan. 21, 2003**

(54) **TIN-COPPER ALLOY ELECTROPLATING BATH**

(75) Inventors: **Isamu Yanada**, Hirakata (JP); **Masanobu Tsujimoto**, Hirakata (JP); **Tetsurou Okada**, Hirakata (JP); **Teruya Oka**, Hirakata (JP); **Hideyuki Tsubokura**, Hirakata (JP)

(73) Assignee: **C. Uyemura & Co., Ltd.**, Osaka (JP)

(*) Notice: This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).

Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/433,887**

(22) Filed: **Nov. 4, 1999**

(65) **Prior Publication Data**

US 2002/0104763 A1 Aug. 8, 2002

(30) **Foreign Application Priority Data**

Nov. 5, 1998 (JP) 10-314210
May 7, 1999 (JP) 11-127648

(51) **Int. Cl.**[7] **C25D 3/58**
(52) **U.S. Cl.** **205/241**; 205/253; 205/254
(58) **Field of Search** 205/241, 253, 205/254

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Primary Examiner—Nam Nguyen
Assistant Examiner—Wesley A. Nicolas
(74) *Attorney, Agent, or Firm*—Sughrue Mion, PLLC

(57) **ABSTRACT**

A tin-copper alloy electroplating bath which comprises a water-soluble tin salt, a water-soluble copper salt, an inorganic or organic acid or a water-soluble salt thereof, and one or more compounds selected from thioamide compounds and thiol compounds. The present invention makes it possible to form a tin-copper alloy deposit, in place of tin-lead alloy plating, on electronic parts such as chips, quartz crystal oscillators, hoops, connector pins, lead frames, bumps, lead pins of packages, and printed circuit boards.

19 Claims, No Drawings

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1	US RE29239 E	3								USPAT
2	US 6582582 B2	5								USPAT
3	US 6562221 B2	4								USPAT
4	US 6562220 B2	5								USPAT
5	US 6508927 B2	11								USPAT
6	US 6500886 B1	13								USPAT
7	US 6478944 B1	13								USPAT

design quality, impartment of electric conductivity, and control of friction and torque coefficients). These is no special limitation to the sources of the above substances to be supplied. Various sources may be used, including metal sulfates, nitrates, hydrochlorides, and other salts, silicate compounds, silane compounds, oxy-acid salts, complex salts, nitrides, oxides, and sulfites. Examples of these combinations are combinations of Si and at least one of alkali metals, alkaline earth metals, transition metals, polyethylene waxes, dyes, alcohols, and resins; and combinations with at least one of resins, conductivity-imparting agents, pigments, torque adjusting agents, alcohols, and ethers.

Detailed Description Text - DETX (53):

Plating was carried out using zinc as the anode, with a solution (pH 4) which contained, all per liter, 288 g white vitriol, 25 g boric acid, 27 g ammonium chloride, 50 g of fine silica powder having a particle diameter of 18 m.mu. ("Bitaseal #1500" made by Taki Seihi K.K.), 0.001 mL nonionic surfactant (polyoxyethylenelaurylamine), and 0.0005 M cationic surfactant (dodecyltrimethylammonium chloride), while thoroughly stirring the solution which had been suspended. Thus a plating layer about 5 .mu.m thick was formed on the side A of test specimens. Partial holidays had occurred at that point. One test specimen was immersed for 35 seconds in a treating solution which contained, all per liter, 5 g ammonium molybdate, 15 g phosphoric acid, 2 g titanium sulfate, 3 g hydrogen peroxide, and 15 g colloidal silica to obtain Test specimen A. Another specimen was immersed for 60 seconds in a treating solution which contained, all per liter, 3 g chromium acetate, 0.1 g sulfuric acid, 0.1 g nitric acid, and 2 g phosphoric acid to obtain Test specimen B. Another specimen was treated in the same way as B and was further immersed for 20 seconds in a treating solution which contained, all per liter, 60 g sodium silicate, 10 g sodium hydroxide, and 0.04 g zinc to obtain Test specimen C.

Claims Text - CLTX (2):

2. A plating solution containing, all per liter, from 2 g to 60 g zinc, from 40 g to 300 g caustic alkali, from 0.01 g to 50 g adsorbent, from 0.002 g to 10 g iron, from 0.002 g to 10 g cobalt, from 0.05 g to 30 g manganese, from 0.001 g to 2 g copper, from 0.005 g to 10 g nickel, from a 0.002 g to 3 g of at least one member selected from the group consisting of molybdenum, tungsten, vanadium, titanium, aluminum, calcium, barium, and tin, and from 0.01 to 30 g aliphatic amine or aliphatic amine polymer.

Current US Cross Reference Classification - CCXR (1):
205/244

Current US Cross Reference Classification - CCXR (2):
205/245

Current US Cross Reference Classification - CCXR (3):
205/246

(12) **United States Patent**
Yamamuro et al.

(10) **Patent No.: US 6,500,886 B1**
(45) **Date of Patent: Dec. 31, 2002**

(54) **SURFACE TREATING AGENT**

(75) Inventors: **Masaaki Yamamuro**, Tokyo (JP); **Mitsuomi Katori**, Tokyo (JP)

(73) Assignee: **Nihon Hyomen Kagaku Kabushiki Kaisha**, Tokyo (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 54 days.

(21) Appl. No.: **09/710,400**

(22) Filed: **Nov. 9, 2000**

(30) **Foreign Application Priority Data**

Nov. 10, 1999 (JP) 11-319339

(51) **Int. Cl.**[7] **C08K 5/34; C25D 3/56**

(52) **U.S. Cl.** **524/99; 524/440; 205/244; 205/245; 205/246**

(58) **Field of Search** 205/244, 245, 205/246; 524/99, 440

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Primary Examiner—Edward J. Cain
(74) *Attorney, Agent, or Firm*—Marshall, Gerstein & Borun

(57) **ABSTRACT**

A plating solution containing zinc, an electrically conductive salt, an adsorbent, and at least one of mono- to hexavalent metal ions. A treatment using either a solution which contains, all per liter, 2–60 g Zn, 40–300 g caustic alkali, 0.01–50 g adsorbent, 0.002–10 g Fe, 0.002–10 g Co, 0.05–30 g Mn, 0.001–2 g Cu, 0.005–10 g Ni, 0.002–3 g of at least one chosen from among Mo, W, V, Ti, Al, Ca, Ba, and Sn, and 0.01–30 g aliphatic amine or aliphatic amine polymer or a solution which contains, all per liter, 2–40 g Zn, 40–170 g caustic alkali, 0.01–50 g adsorbent, either 0.001–3 g Fe and 0.001–3 g Co or 0.005–5 g Fe and 0.005–5 g Ni, and 0.01–30 g aliphatic amine or aliphatic amine polymer.

20 Claims, 1 Drawing Sheet

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8	US 6436269 B1	8								USPAT
9	US 6322686 B1	7								USPAT
10	US 6251253 B1	4								USPAT
11	US 6248228 B1	4								USPAT
12	US 6183619 B1	5								USPAT
13	US 6183545 B1	7								USPAT

Brief Summary Text - BSTX (20):

An aqueous solution according to the invention for the reductive deposition of metals contains one or two or more types of metals selected from the group consisting of copper, silver, gold, zinc, cadmium, indium, germanium, tin, lead, arsenic, antimony, bismuth, chromium, molybdenum, manganese, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum. Where codeposition with such a metal or metals is desired, the solution may further contain one or two or more compounds containing phosphorus, boron, or tungsten.

Brief Summary Text - BSTX (25):

The aqueous solution of the invention for the reductive deposition of metals may contain, depending on its intended use, any of known reducing agents, surfactants, smoothening agents, semi-brighteners, brighteners, stabilizing auxiliary complexing agents, masking complexing agents, pH buffers, conductive salts and/or any of antioxidants or other additives.

Brief Summary Text - BSTX (27):

The compounds that can be suitably used as surfactants are the cationic, anionic, nonionic, and amphoteric surfactants usually used in plating baths. They are used singly or as a mixture as desired.

Brief Summary Text - BSTX (28):

As suitable surfactants, cationic surfactants include tetra-lower alkylammonium halides, alkyltrimethylammonium halides, hydroxyethyl alkyl imidazoline, polyoxyethylene alkyl methyl ammonium halides, alkylbenzalkonium halides, dialkyldimethyl ammonium halides, alkyldimethyl benzyl ammonium halides, alkylamine hydrochlorides, alkylamine acetates, alkylamine oleates, alkylaminoethyl glycine, and alkylpyridinium halides.

Brief Summary Text - BSTX (29):

Among anionic surfactants are alkyl(or formalin condensate)-.beta.-naphthalenesulfonic acids (or their salts), fatty acid soaps, alkyl sulfonates, .alpha.-olefin sulfonates, alkylbenzenesulfonates, alkyl(or alkoxy)naphthalenesulfonates, alkyldiphenyl ether disulfonates, alkyl ether sulfonates, alkylsulfuric esters, polyoxyethylene alkyl ether sulfuric esters, polyoxyethylene alkyl phenol ether sulfuric esters, higher alcohol phosphoric monoesters, polyoxyalkylene alkyl ether phosphoric acids (phosphates), polyoxyalkylene alkyl phenyl ether phosphates, polyoxyalkylene phenyl ether phosphates, polyoxyethylene alkyl ether acetates, alkanoyl sarcosines, alkanoyl sarcosinates, alkanoyl methylalanine salts, alkyl sulfoacetates, acyl methyl taurines, alkyl fatty acid glycerin sulfuric esters, hardened coconut oil fatty acid glyceryl sulfates, alkyl sulfocarboxylic esters, alkyl sulfosuccinates, dialkyl sulfosuccinates, alkyl polyoxyethylene sulfosuccinates, and sodium (or ammonium or TEA) sulfosuccinic monooleylamides.

Brief Summary Text - BSTX (30):

Nonionic surfactants are, e.g., polyoxyalkylene alkyl ethers (or esters), polyoxyalkylene phenyl (or alkylphenyl) ethers, polyoxyalkylene naphthyl (or alkylnaphthyl) ethers, polyoxyalkylene styrenated phenyl ethers (or surfactants prepared by further adding a polyoxyalkylene to the phenyl group), polyoxyalkylene bisphenol ethers, polyoxyethylenepolyoxypropylene block polymers, polyoxyalkylene sorbitan fatty acid esters, polyoxyalkylene sorbitol

(12) **United States Patent**
Okuhama et al.

(10) **Patent No.: US 6,183,545 B1**
(45) **Date of Patent: Feb. 6, 2001**

(54) **AQUEOUS SOLUTIONS FOR OBTAINING METALS BY REDUCTIVE DEPOSITION**

(75) Inventors: **Yoshiaki Okuhama; Takao Takeuchi; Masakazu Yoshimoto; Shigeru Takatani; Emiko Tanaka; Masayuki Nishino; Yuji Kato; Yasuhito Kohashi; Kyoko Kubo; Tetsuya Kondo; Keiji Shiomi; Keigo Obata, all of Akashi; Mitsuo Komatsu, Ibaraki; Hidemi Nawafune, Takatsuki, all of (JP)**

(73) Assignee: **Daiwa Fine Chemicals Co., Ltd.,** Hyogo-ken (JP)

(*) Notice: Under 35 U.S.C. 154(b), the term of this patent shall be extended for 0 days.

(21) Appl. No.: **09/340,894**

(22) Filed: **Jun. 28, 1999**

(30) **Foreign Application Priority Data**

Jul. 14, 1998 (JP) 10-198763

(51) **Int. Cl.**[7] **C23C 18/31**; C23C 18/32; C23C 18/38; C23C 18/42; C23C 18/48; C23C 18/50; C23C 18/54; C23C 3/20; C23C 3/22; C23C 3/26; C23C 3/30; C23C 3/36; C23C 3/38; C23C 3/46; C23C 3/48; C23C 3/52; C23C 3/54; C23C 3/56; C25D 3/10; C25D 3/12

(52) **U.S. Cl.** **106/1.18**; 106/1.19; 106/1.21; 106/1.22; 106/1.23; 106/1.24; 106/1.25; 106/1.26; 106/1.27; 106/1.28; 106/1.29; 205/239; 205/240; 205/241; 205/242; 205/243; 205/244; 205/245; 205/246; 205/247; 205/250; 205/251; 205/253; 205/258; 205/259; 205/262; 205/263; 205/264; 205/265; 205/267; 205/269; 205/270; 205/271; 205/281; 205/290; 205/296; 205/299; 205/302; 205/311; 205/315

(58) **Field of Search** 106/1.18–1.29; 205/239–247, 250, 251, 253, 258, 259, 262–265, 267, 269–271, 281, 290, 296, 299, 302, 311, 315

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Primary Examiner—Helene Klemanski
(74) *Attorney, Agent, or Firm*—Akin, Gump, Strauss, Hauer & Feld, L.L.C.

(57) **ABSTRACT**

An aqueous solution for the reductive deposition of metals comprising, besides water,

(A) a phosphine of the general formula (1)

(1)

in which R_1, R_2, and R_3 denote lower alkyl groups, at least one of which being hydroxy-or amino-substituted lower alkyl group, and

(B) a soluble compound of a metal or a compound of a metal solubilized through the formation of a soluble complex by said phosphine.

12 Claims, No Drawings

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9	US 6322686 B1	7				☑				USPAT
10	US 6251253 B1	4				☑				USPAT
11	US 6248228 B1	4				☑				USPAT
12	US 6183619 B1	5				☑				USPAT
13	US 6183545 B1	7				☑				USPAT
14	US 6179985 B1	3				☑				USPAT
15	US 5951841 A	13				☑				USPAT

US-PAT-NO: 5951841

DOCUMENT-IDENTIFIER: US 5951841 A
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TITLE: Electroplating baths salts of aromatic hydroxy compounds and their use as brighteners

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Brief Summary Text - BSTX (4):
In the electrodeposition of metals or alloys, in particular of zinc or tin or zinc alloys or tin alloys, onto metallic substrates, such as shaped metal articles or metallated plastic shaped articles, from aqueous acidic solution, a bright coating is frequently desirable in order to give the electroplated article an advantageous decorative appearance. Thus, in addition to the corrosion-inhibiting effect or an effect which improves the mechanical properties of the shaped article, a decorative effect is often desirable. In order to obtain the desired effects, it is essential that the electroplating baths contain certain assistants, since otherwise the metal coatings being deposited from acidic solution are generally dull and frequently also irregular. A group of such assistants for acidic electroplating baths comprises, for example, conductive salts which are used for improving the conductivity of the baths. Another group of assists comprises the brighteners.

Brief Summary Text - BSTX (177):
Preferred metal salts are zinc salts and tin salts.

Brief Summary Text - BSTX (181):
The novel aqueous acidic electroplating baths have the usual compositions with regard to the other components. They contain, for example, 50-150 g/l of zinc chloride or the equivalent amount of zinc sulfate. If alloys of zinc, for example with cobalt and/or nickel and/or iron, are to be deposited onto metallic shaped articles, the baths additionally contain, as a rule, 1-30 g/l of cobalt sulfate and/or nickel sulfate and/or iron sulfate or the equivalent amount of another, water-soluble cobalt and/or nickel and/or iron salt. It is also possible to use the corresponding tin salts in equivalent amounts.

Brief Summary Text - BSTX (183):
A further conventional component of the novel aqueous acidic electroplating baths comprises surfactants or wetting agents, in particular nonionic and ionic surfactants, which act as auxiliary brighteners. Suitable nonionic surfactants are disclosed, for example, in British Patent 1,149,106. These are adducts of ethylene oxide with fatty alcohols, for example with C.sub.8 -C.sub.18 -alcohols, or adducts of ethylene oxide with phenol or alkylphenols, in particular with nonylphenol. As a rule, 5-100 mol of ethylene oxide are subjected to an addition reaction per mole of alcohol or phenol. Polyoxyalkylated naphthols may also be added.

Brief Summary Text - BSTX (184):
Further useful nonionic surfactants include poly(alkyleneimines).

another, water-soluble cobalt and/or nickel and/or iron salt. It is also possible to use the corresponding tin salts in equivalent amounts.

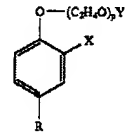
A further conventional component of the baths comprises conductive salts, in particular sodium salts, potassium salts and ammonium salts. A suitable conductive salt is potassium chloride, which is usually present in a concentration of 100–250 g/l in a novel electroplating bath. Other conductive salts are, for example, ammonium chloride and sodium chloride, which are usually used in a concentration of 10–150 g/l

A further conventional component of the novel aqueous acidic electroplating baths comprises surfactants or wetting agents, in particular nonionic and ionic surfactants, which act as auxiliary brighteners. Suitable nonionic surfactants are disclosed, for example, in British Patent 1,149,106. These are adducts of ethylene oxide with fatty alcohols, for example with C_8–C_{18}-alcohols, or adducts of ethylene oxide with phenol or alkylphenols, in particular with nonylphenol. As a rule, 5–100 mol of ethylene oxide are subjected to an addition reaction per mole of alcohol or phenol. Polyoxyalkylated naphthols may also be added.

Further useful nonionic surfactants include poly(alkyleneimines). Poly(alkyleneimines) may be used as such or they may be reacted with a cyclic carbonate which consists of carbon, hydrogen and oxygen atoms. A description of the preparation of such compounds is disclosed in U.S. Pat. No. 2,824,857.

Suitable anionic surfactants are disclosed, for example, in U.S. Pat. No. 3,787,296. These are mainly sulfated polyethers, which are obtainable, for example, by an addition reaction of ethylene oxide with fatty alcohols, fatty amines, amides of C_6–C_{10}-carboxylic acids and relatively long-chain fatty acids and a subsequent sulfonation in each case. Sulfonates of polyalkylene oxides or block copolymers of ethylene oxide and propylene oxide are also used as anionic surfactants.

A further group of anionic surfactants is disclosed in EP-B-115 020. Sulfonated and sulfatedalkylphenolethoxyl of the general formula



where R is C_4–C_{20}-alkyl, X and Y are each a radical of the formula $—SO_3H$ or $—SO_3Me$ and Me is ammonium, an alkali metal or one equivalent of an alkaline earth metal or zinc atom and p is 5–50, are described.

In addition to such compounds, other suitable anionic surfactants are the sulfonated and sulfated products whose polyether chain contains 1–25 propylene oxide or butylene oxide units.

DE-C-38 39 824 discloses anionic additives based on monobasic and polybasic ethersulfonic acids. These are prepared by individual or combined sulfopropylation and/or sulfobutylation of the following hydroxyl-containing compounds:

a) block polymers of ethylene oxide and/or glycidol with propylene oxide and/or butylene oxide;

b) monohydric or polyhydric saturated or unsaturated aliphatic alcohols and monohydric or polyhydric, alkylated or nonalkylated phenols or naphthols, including their alkoxylates.

The advantage of the sulfonated and sulfated alkylphenol alkoxylates is that they have an extremely high cloud point so that the electrolytic deposition of the metal, in particular of zinc, can be carried out not only at 20–30° C. but also at 30–90° C., preferably 40–50° C.

Further suitable surfactants include phenol/formaldehyde condensates and naphthalenesulfonic acid/formaldehyde condensates.

In addition to the stated surfactants, polyethylene glycols having molecular weights 200–1000 g/mol are also suitable auxiliary brighteners.

The surfactants and other auxiliary brighteners are used in the novel aqueous acidic electroplating baths usually in amounts of 1–20, preferably 2–15, g/l. It is also possible to use a mixture of a plurality of surfactants, or auxiliary brighteners.

The pH of the novel aqueous acidic electroplating baths is, as a rule, 3–7, preferably 4–5. It is established, for example, by adding acids, for example conventional mineral acids, such as sulfuric acid or hydrochloric acid.

The present invention furthermore relates to a process for the electroplating of shaped articles, which comprises

1. bringing a shaped article into contact with a novel acidic electroplating bath and

2. carrying out electroplating.

By means of the novel process, for example, shaped articles comprising metals, mainly comprising iron or steel, are electroplated in order to protect them from corrosion and simultaneously to give them great brightness. The novel acidic electroplating baths used for this purpose give, with the entire, technically relevant current density range, very bright and ductile metal coatings, for example zinc coatings, the quality of which corresponds or is even superior to the quality of the coatings obtainable using benzylideneacetone according to the prior art.

Synthesis Examples for compounds of the formula are I and II and Use Examples for novel acidic electroplating baths are described below.

IV. EXAMPLES

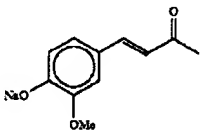
The subjects of the present invention a illustrated by the following examples, in which further preferred individual feature of the invention are described.

1. Synthesis Examples

Synthesis Examples for some of the novel compounds of the formulae I and II are described below.

Example 1

Preparation of the sodium salt of vanillideneacetone:



4.9 g (0.032 mol) of vanillin were dissolved in 15 ml of acetone, and 5.3 ml of 50% strength sodium hydroxide solution were added. Thereafter, 10 ml of water were added and stirring was carried out for 20 hours at room temperature. The precipitated residue was washed with acetone and dried. 7 g (corresponding to a yield of 95%) of the title compound were obtained in the form of an orange-yellow solid The purity of the product was >97%.

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17	US 5618402 A	5				☑				USPAT

US-PAT-NO: 5618402

DOCUMENT-IDENTIFIER: US 5618402 A

TITLE: Tin-zinc alloy electroplating bath and method for electroplating using the same

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Abstract Text - ABTX (1):
A tin-zinc alloy electroplating bath comprises an amphoteric surfactant, a water-soluble stannous salt, a water-soluble zinc salt and a balance of water. When the tin-zinc alloy plating bath of the present invention is used, the formed coating film comprises a uniform alloy composition even in case where the current density varies over a wide range. Therefore, the coating film having the uniform alloy composition can be formed even on the substance having a complicated shape and the chromate treatment becomes satisfactory. As a result, the effect of the coating is improved, the resultant product is stable and the productivity is improved. Thus the tin-zinc alloy coating film having a high quality can be provided.

TITLE - TI (1):
Tin-zinc alloy electroplating bath and method for electroplating using the same

Brief Summary Text - BSTX (2):
The present invention relates to a tin-zinc alloy electroplating bath and a method for electroplating using the same. In particular, the present invention relates to a tin-zinc alloy electroplating bath capable of stably forming a coating of a uniform alloy composition by keeping the plating alloy composition from the influence of the current density.

Brief Summary Text - BSTX (3):
The tin-zinc alloy electroplating method attracted attention, and recently has come to be widely used as an industrial plating method for automobile parts and electronic parts, since the electroplated products have excellent corrosion resistance, aqueous salt solution resistance and solderability.

Brief Summary Text - BSTX (4):
The plating baths heretofore proposed for the tin-zinc alloy electroplating include, for example, an alkaline cyanide bath, pyrophosphate bath, borofluoride bath, sulfonate bath, carboxylate bath and cyanide-free alkaline bath. Some of them are practically used.

Brief Summary Text - BSTX (5):
A defect common to the conventional tin-zinc alloy PLATING BATHS is that the current density exerts a strong influence on the composition of the plating alloy. Namely, even when the current density during the plating is fixed, the current density distribution on the surface of the substance to be plated is not always even and, therefore, the composition of the plating alloy is

United States Patent [19]

Sakurai et al.

[11] **Patent Number: 5,618,402**

[45] **Date of Patent: Apr. 8, 1997**

[54] **TIN-ZINC ALLOY ELECTROPLATING BATH AND METHOD FOR ELECTROPLATING USING THE SAME**

[75] Inventors: **Hitoshi Sakurai**, Matsudo; **Tadahiro Ohmura**, Funabashi, both of Japan

[73] Assignee: **Dipsol Chemicals Co., Ltd.**, Tokyo, Japan

[21] Appl. No.: **180,345**

[22] Filed: **Jan. 12, 1994**

[51] **Int. Cl.**[6] **C25D 3/56**; C25D 3/60

[52] **U.S. Cl.** **205/244**; 205/252; 205/253; 205/254

[58] **Field of Search** 205/244, 252, 205/253, 254; 106/1.05, 1.25, 1.29

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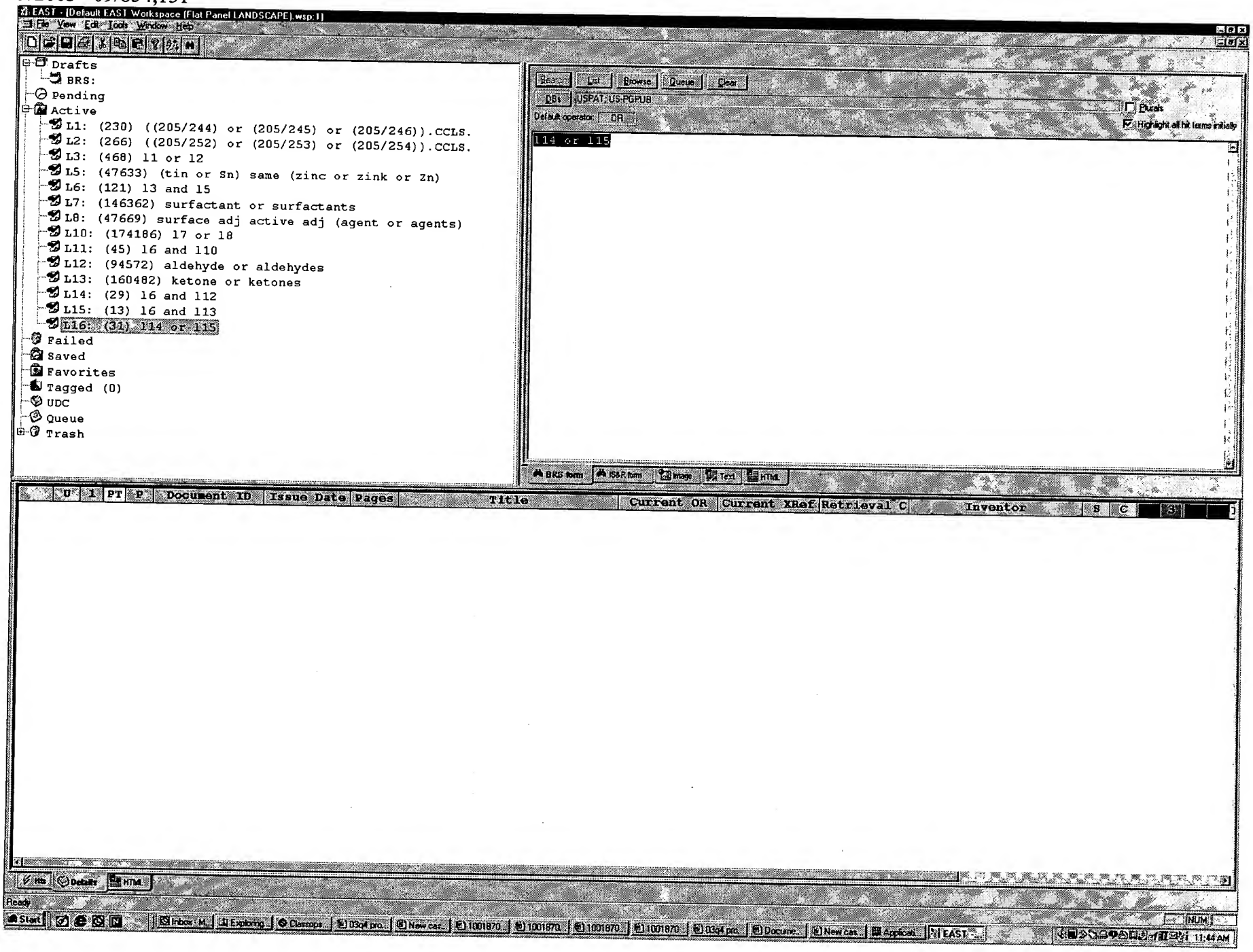
Primary Examiner—Kathryn L. Gorgos
Assistant Examiner—Edna Wong
Attorney, Agent, or Firm—Oblon, Spivak, McClelland, Maier & Neustadt, P.C.

[57] **ABSTRACT**

A tin-zinc alloy electroplating bath comprises an amphoteric surfactant, a water-soluble stannous salt, a water-soluble zinc salt and a balance of water. When the tin-zinc alloy plating bath of the present invention is used, the formed coating film comprises a uniform alloy composition even in case where the current density varies over a wide range. Therefore, the coating film having the uniform alloy composition can be formed even on the substance having a complicated shape and the chromate treatment becomes satisfactory. As a result, the effect of the coating is improved, the resultant product is stable and the productivity is improved. Thus the tin-zinc alloy coating film having a high quality can be provided.

16 Claims, No Drawings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L1: (230) ((205/244) or (205/245) or (205/246)).CCLS.
L2: (266) ((205/252) or (205/253) or (205/254)).CCLS.
L3: (468) l1 or l2
L5: (47633) (tin or Sn) same (zinc or zink or Zn)
L6: (121) l3 and l5
L7: (146362) surfactant or surfactants
L8: (47669) surface adj active adj (agent or agents)
L10: (174186) l7 or l8
L11: (45) l6 and l10
L12: (94572) aldehyde or aldehydes
L13: (160482) ketone or ketones
L14: (29) l6 and l12
L15: (13) l6 and l13
L16: (31) l14 or l15
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Default operator:
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2	US 6562221 B2	4											☑				USPAT
3	US 6508927 B2	11											☑				USPAT
4	US 6500886 B1	13											☑				USPAT
5	US 6436269 B1	8											☑				USPAT
6	US 6322686 B1	7											☑				USPAT
7	US 5951841 A	13											☑				USPAT

US-PAT-NO: 5951841

DOCUMENT-IDENTIFIER: US 5951841 A
See image for Certificate of Correction

TITLE: Electroplating baths salts of aromatic hydroxy compounds and their use as brighteners

---------- KWIC ---------

Brief Summary Text - BSTX (4):
In the electrodeposition of metals or alloys, in particular of zinc or tin or zinc alloys or tin alloys, onto metallic substrates, such as shaped metal articles or metallated plastic shaped articles, from aqueous acidic solution, a bright coating is frequently desirable in order to give the electroplated article an advantageous decorative appearance. Thus, in addition to the corrosion-inhibiting effect or an effect which improves the mechanical properties of the shaped article, a decorative effect is often desirable. In order to obtain the desired effects, it is essential that the electroplating baths contain certain assistants, since otherwise the metal coatings being deposited from acidic solution are generally dull and frequently also irregular. A group of such assistants for acidic electroplating baths comprises, for example, conductive salts which are used for improving the conductivity of the baths. Another group of assists comprises the brighteners.

Brief Summary Text - BSTX (5):
U.S. Pat. No. 3,694,330 (Reissue 27 999) discloses acidic electroplating zinc baths which contain ammonium salts and, as brighteners, aromatic carbonyl compounds. Aromatic carboxylic acids and aromatic aldehydes and ketones are mentioned as the latter. Explicitly mentioned are, inter alia, cinnamic acid, cinnamaldehyde, benzoic acid, benzalacetone and ethyl benzoylacetate.

Brief Summary Text - BSTX (6):
U.S. Pat. No. 4,222,908 describes acidic electroplating zinc baths which contain sulfamate ions and, as brighteners, aromatic carbonyl compounds. Aromatic aldehydes and ketones are mentioned, including benzalacetone as a preferred substance.

Brief Summary Text - BSTX (177):
Preferred metal salts are zinc salts and tin salts.

Brief Summary Text - BSTX (181):
The novel aqueous acidic electroplating baths have the usual compositions with regard to the other components. They contain, for example, 50-150 g/l of zinc chloride or the equivalent amount of zinc sulfate. If alloys of zinc, for example with cobalt and/or nickel and/or iron, are to be deposited onto metallic shaped articles, the baths additionally contain, as a rule, 1-30 g/l of cobalt sulfate and/or nickel sulfate and/or iron sulfate or the equivalent amount of another, water-soluble cobalt and/or nickel and/or iron salt. It is also possible to use the corresponding tin salts in equivalent amounts.

United States Patent [19]

Wehlage et al.

[11] **Patent Number: 5,951,841**

[45] **Date of Patent: Sep. 14, 1999**

[54] **ELECTROPLATING BATHS SALTS OF AROMATIC HYDROXY COMPOUNDS AND THEIR USE AS BRIGHTENERS**

[75] Inventors: **Thomas Wehlage**, Speyer; **Ulrich Schröder**, Frankenthal; **Alfred Oftring**, Bad Dürkheim, all of Germany

[73] Assignee: **BASF Aktiengesellschaft**, Ludwigshafen, Germany

[21] Appl. No.: **08/860,301**

[22] PCT Filed: **Dec. 22, 1995**

[86] PCT No.: **PCT/EP95/05090**

§ 371 Date: **Oct. 6, 1997**

§ 102(e) Date: **Oct. 6, 1997**

[87] PCT Pub. No.: **WO96/20152**

PCT Pub. Date: **Jul. 4, 1996**

[30] **Foreign Application Priority Data**

Dec. 23, 1994 [DE] Germany 44 46 329

[51] **Int. Cl.**[6] **C25D 3/00**

[52] **U.S. Cl.** **205/261**; 205/253; 205/303; 205/314; 549/287; 558/401; 560/51; 564/123; 568/308

[58] **Field of Search** 205/253, 302, 205/303, 307, 308, 311, 312, 314, 261; 106/1.05; 549/287; 558/401; 568/308; 560/51; 564/123

[56] **References Cited**

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4,242,182	12/1980	Popescu	205/303
4,422,908	12/1983	Welch .	
5,421,990	6/1995	Haba et al. .	

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29 48 261	7/1980	Germany .
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Koichi Araki, Hironobu Hashimoto, and Juji Yoshimura. "Synthetic Studies on Glycocinnamoylspermidines. Synthesis of a key intermediate of the Diaminohexose moiety."Carbohydr. Res., 109, 143-60 (English). Abstract taken from Chemical Abstracts 98:54363, 1982.

Patent Abstracts of Japan , vol. 14, No. 43 (C-0681), Nov. 6, 1989, Jp 1-275-552, Apr. 28 1988.

Primary Examiner—Kathryn Gorgos
Assistant Examiner—Wesley A. Nicolas
Attorney, Agent, or Firm—Oblon, Spivak, McClelland, Maier & Neustadt, P.C.

[57] **ABSTRACT**

Salts of aromatic hydroxy compounds are used as brighteners in acidic electroplating baths. Furthermore, acidic electroplating baths for the electrolytic deposition of metallic layers onto shaped articles comprise, as brighteners, at least one novel salt of an aromatic hydroxy compound. Finally, shaped articles are electroplated by a process using the novel acidic electroplating baths.

17 Claims, No Drawings

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3	US 6508927 B2	11				☑				USPAT
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5	US 6436269 B1	8				☑				USPAT
6	US 6322686 B1	7				☑				USPAT
7	US 5951841 A	13				☑				USPAT
8	US 5618402 A	5				☑				USPAT

density No. Other additives Amount plated product 0.2 A/dm.sup.2 1.5 A/dm.sup.2 5 A/dm.sup.2

None -- Dull 31.2 40.3 43.0 2 Aromatic aldehyde 0.1 g/l Semiglossy 28.0 38.6 39.2 3 None -- Dull 25.5 38.8 41.2 4 None -- Dull 20.7 35.6 34.7 5 DIPSOL .RTM. DG-FR-7 0.1 g/l Semiglossy 20.1 35.1 35.7 6 None -- Dull 21.3 38.4 39.4 7 DIPSOL .RTM. SZ-240S 8 ml/l Semiglossy 20.5 35.1 38.5 8 None -- Dull 27.0 37.6 41.0 9 None -- Dull 21.5 34.9 37.7 10 DIPSOL .RTM. SZ-240S 8 ml/l Semiglossy 19.3 34.4 38.2 11 Polyoxyethylene 5 g/l Semiglossy 20.5 35.9 39.3 laurylamine (15 mol ethylene oxide adduct) 12 None -- Dull 23.3 36.6 39.0 13 None -- Semiglossy 25.0 38.9 40.5 14 Aliphatic amine/ 2 ml/l Semiglossy 10.3 11.8 12.3 organic acid ester/ phthalic anhydride reaction product 15 None -- Dull 54.6 68.6 74.6 16 Epoxy compound/ 2 g/l Semiglossy 67.9 80.3 82.4 propylene glycol reaction product 31 DIPSOL .RTM. SZ-240S 8 ml/l Semiglossy 12 35 37.5 32 DIPSOL .RTM. SZ-240S 8 ml/l Semiglossy 9.0 48.3 50.6 33 Polyoxyethylene 5 g/l Semiglossy 8.5 17.0 33.8 laurylamine (15 mol ethylene oxide adduct) 34 Polyoxyethylene 5 g/l Semiglossy 9 35 45 laurylamine (15 mol ethylene oxide adduct) 35 None -- Spongy surface -- -- -- 36 Aliphatic amine/ 2 ml/l Semiglossy 8.4 15.0 19.7 organic acid ester/ phthalic anhydride/ reaction product 37 Polyethylene glycol 5 g/l Semiglossy 18.1 40.2 51.9

Detailed Description Paragraph Table - DETL (3):

No. 14 15 16 36 37

Tin 20 10 5 20 10 Zinc 1 20 20 1 20

Claims Text - CLTX (1):

1. A tin-zinc alloy electroplating bath which comprises:

Claims Text - CLTX (8):

2. The tin-zinc alloy electroplating bath of claim 1 wherein the amphoteric surfactant is an imidazoline.

Claims Text - CLTX (9):

3. The tin-zinc alloy electroplating bath of claim 1 wherein the amphoteric surfactant is present in an amount of 0.3 to 15 g/l.

Claims Text - CLTX (10):

4. The tin-zinc alloy electroplating bath of claim 1 wherein the water-soluble stannous salt is present in an amount of 5 to 50 g/l in terms of metallic tin.

Claims Text - CLTX (11):

5. The tin-zinc alloy electroplating bath of claim 1 wherein the water-soluble zinc salt is present in an amount of 25 to 40 g/l in terms of metallic zinc.

Claims Text - CLTX (12):

6. The tin-zinc alloy electroplating bath of claim 1 which is a

wherein R^7 represents an alkyl group having 8 to 20 carbon atoms.

The amphoteric surfactants of glycine type are preferably those having a structure of the following formula (5) or (6):

$$R^8—NHCH_2CH_2NHCH_2COOH \quad (5)$$

$$(R^8—NHCH_2CH_2)_2NCH_2COOH \quad (6)$$

wherein R^8 represents an alkyl group having 8 to 20 carbon atoms.

The amphoteric surfactants of amide type are preferably those having a structure of the following formula (7):

$$R^9—CONHCH_2CH_2NHCH_2COOna \quad (7)$$

wherein R^9 represents an alkyl group having 8 to 20 carbon atoms.

These amphoteric surfactants can be used either singly or in combination of two or more of them.

The tin-zinc alloy electroplating baths of the present invention include, for example, an alkaline cyanide bath, pyrophosphate bath, borofluoride bath, silicofluoride bath, sulfonate bath, carboxylate bath, cyanide-free alkaline bath, gluconate bath and organic acid bath. The bath contains a water soluble stannous salt such as stannous sulfate in an amount of usually 1 to 100 g/l (in terms of metallic tin), preferably 5 to 50 g/l, and a water soluble zinc salt such as zinc sulfate in an amount of usually 0.2 to 80 g/l (in terms of metallic zinc), preferably 25 to 40 g/l. Particularly preferred is the cyanide-free bath. The bath can contain 40 to 400 g/l of a carboxylic acid having 1 to 15 carbon atoms, preferably 3 to 7 carbon atoms such as citric acid or gluconic acid, 30 to 300 g/l of pyrophosphoric acid or 20 to 400 g/l of sulfamic acid. The pH of the bath ranges from 3 to 10.

An ordinary brightener or additive can be added to the plating bath. For example, 0.1 to 20 g/l of a water-soluble brightener obtained by reacting phthalic anhydride with a reaction product of an aliphatic amine and an organic acid ester can be added to the bath.

When the plating bath of the present invention is used, an intended tin-zinc alloy coating having a thickness of, for example, 0.5 μm to 0.5 mm can be formed by the electroplating on a metal such as iron, nickel, copper or an alloy of them. Further, by varying the ratio of tin to zinc in the plating bath, various tin-zinc alloy coating compositions can be obtained. For example, a composition having a zinc content of 5 to 5% by weight is used for the electric contact or the like; a composition having a zinc content of 15 to 45% by weight is used when a high resistance to an aqueous salt solution and to corrosion is necessitated; and a composition having a zinc content of 45 to 90% by weight is used for the formation of a coating having a high corrosion resistance which is to be exposed to air.

Although the electroplating conditions are not particularly limited, the plating bath temperature is preferably 10° to 70° C., more preferably 10° to 40° C. and the current density is preferably 0.1 to 10 A/dm². The time period for the electroplating is not limited, but preferably 1 minutes to 2 hours, more preferably 5 minutes to 1 hour. In this connection, the substrate is a cathode and tin-zinc alloy is an anode. A

weight ratio of tin to zinc in the anode is optional but preferably the ratio may be the same as in the alloy composition formed on the substrate.

The coating formed by using the electroplating bath of the present invention can be treated with a chromate by an ordinary method. The treatment with the chromate can be conducted by, for example, a method described in J. P. KOKOKU No. Sho 38-1110.

When the tin-zinc alloy plating bath of the present invention is used, the formed coating film comprises a uniform alloy composition even in case the current density varies over a wide range. Therefore, the coating film having the uniform alloy composition can be formed even on the substrate having a complicated shape, and the chromate treatment becomes satisfactory. As a result, the effect of the coating film is improved, the resultant product is stable and the productivity is improved. Thus the tin-zinc alloy coating film having a high quality can be provided.

The following Examples will further illustrate the present invention. The composition of the plating bath and the plating conditions can be changed depending on the object.

EXAMPLE 1

The basic tin-zinc alloy plating bath used in the Examples of the present invention are given in Table 1.

TABLE 1

Basic plating bath used in Examples		
Bath		
Citrate bath	Gluconate bath	Pyrophos bath
Bath composition		
Stannous sulfate (40 g/l)	Stannous sulfate (40 g/l)	Stannous pyrophosphate (20 g/l)
Zinc sulfate (40 g/l)	Zinc sulfate (40 g/l)	Zinc pyrophosphate (40 g/l)
Citric acid (100 g/l)	Gluconic acid (120 g/l)	Pyrophosphoric acid (100 g/l)
Ammonium sulfate (80 g/l)	Ammonium sulfate (80 g/l)	
pH adjuster		
Sodium hydroxide or ammonia water	Sodium hydroxide or ammonia water	Potassium hydroxide
Plating bath temp.:	Citrate bath and gluconate bath: 25° C. Pyrophosphate bath 60° C.	

In this Example, the electroplating was conducted at the above-mentioned bath temperature for 10 to 60 min, wherein an iron sheet was used as the cathode and a tin-zinc alloy sheet (weight ratio of tin to zinc is 90/50) was used as the anode and the current density was 0.2 to 5 A/dm².

The compositions of the tin-zinc alloy plating bath containing the amphoteric surfactant used in the Example and also of the coating alloy film obtained from the bath are given in Table 2.

For comparison, the compositions of the amphoteric surfactant-free plating bath and also of the coating alloy film obtained from the bath are also given in Table 2.

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14	US 4581110 A	6				☑				USPAT
15	US 4488942 A	10				☑				USPAT
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17	US 4384930 A	10				☑				USPAT
18	US 4331518 A	5				☑				USPAT
19	US 4168223 A	7				☑				USPAT

Abstract Text - ABTX (1):

An electroplating bath for depositing tin or a tin alloy with satisfactory brightness, which comprises a mother bath of a pH-value ranging from 4 to 8 and containing citric acid or its salt, an ammonium salt and a water-soluble polymer as a brightener. The bath may further comprise an aldehyde compound as a co-brightener.

Brief Summary Text - BSTX (6):

In the printed specification for said USSR Inventor's Certificate, there is a disclosure that dextrine and gelatine are added as brighteners to attain a finer and crystalline tin-zinc alloy deposition with a brightness. However, the "brightness" to be attained by this Inventor's Certificate process is of the degree "dull" or "mat" among the brightness degrees comprising bright (mirror bright), semi-bright, dull, mat and dendrite.

Brief Summary Text - BSTX (7):

In order to improve the brightness, one of the present inventors has proposed together with others a brightener for tin-zinc alloy electroplatings, which is a water-soluble polymer obtained by reacting an aliphatic amine with an organic acid ester and then further reacting the reaction product with phthalic acid anhydrides, or adding to the final reaction product an aromatic aldehyde as a co-brightener (Jap. Pat. Appln. No. 148 687/1974 which was early opened under the number of 75 632/1976). The brightener is advantageous in attaining a "bright" or "semi-bright" tin-zinc alloy electroplating regardless of a kind of the metal to be plated or an electroplating bath to be employed. The brightener, however, has a practical disadvantage that the range of working current density required during the electroplating is relatively narrow.

Brief Summary Text - BSTX (13):

In addition to the water soluble polymer, at least one aldehyde compound may be added as a co-brightener. As the aldehyde compounds, formaldehyde, acetaldehyde, propionaldehyde, glyoxal, succindialdehyde, caproaldehyde, aldol or the like aliphatic one and benzaldehyde, p-tolualdehyde, salicylaldehyde, veratraldehyde, anisaldehyde, piperonal, vanillin or the like aromatic one my be employed solely or as a mixture thereof. These aldehyde compounds themselves do not show any effect as the brightener when using either solely or in the form of a mixture thereof but serve to give a superior brightness to be classified as "bright" or "mirror bright" to the tin or tin-alloy electrodeposition when the same is used in combination with the water soluble polymer as main brightener. In this connection, please note that if no aldehyde compound is added to the electroplating bath, tin or tin-alloy film to be deposited on a base material assumes a brightness classified as "semi-bright" or "dull".

Brief Summary Text - BSTX (20):

The aldehyde compound as co-brightener is added to the mother bath in an amount of 0.1 to 0.5 g/l. The excessive addition does not give any bad influence but is meaningless.

Detailed Description Paragraph Table - DETL (1):

1) Tin Plating Anode: Sn plate

Composition of mother bath: $SnSO_4$ 50 g/l Ammonium citrate 100 g/l

United States Patent [19]

Igarashi et al.

[11] **4,168,223**

[45] **Sep. 18, 1979**

[54] **ELECTROPLATING BATH FOR DEPOSITING TIN OR TIN ALLOY WITH BRIGHTNESS**

[75] Inventors: **Shuji Igarashi; Yoshikazu Fujisawa; Toshio Igarashi, all of Tokyo, Japan**

[73] Assignee: **Dipsol Chemicals Co., Ltd., Tokyo, Japan**

[21] Appl. No.: **960,944**

[22] Filed: **Nov. 15, 1978**

[30] **Foreign Application Priority Data**

Nov. 16, 1977 [JP] Japan 52-136730
Nov. 16, 1977 [JP] Japan 52-136731

[51] Int. Cl.[2] C25D 3/32; C25D 3/60

[52] U.S. Cl. ..... 204/43 S; 204/44; 204/54 R

[58] Field of Search ..... 204/43 S, 54 R, 54 L, 204/44, 120, 123; 106/1.25, 1.22

[56] **References Cited**

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3,892,637	7/1975	Pohl	204/43 S X
3,905,878	9/1975	Dohi et al.	204/43 S

FOREIGN PATENT DOCUMENTS

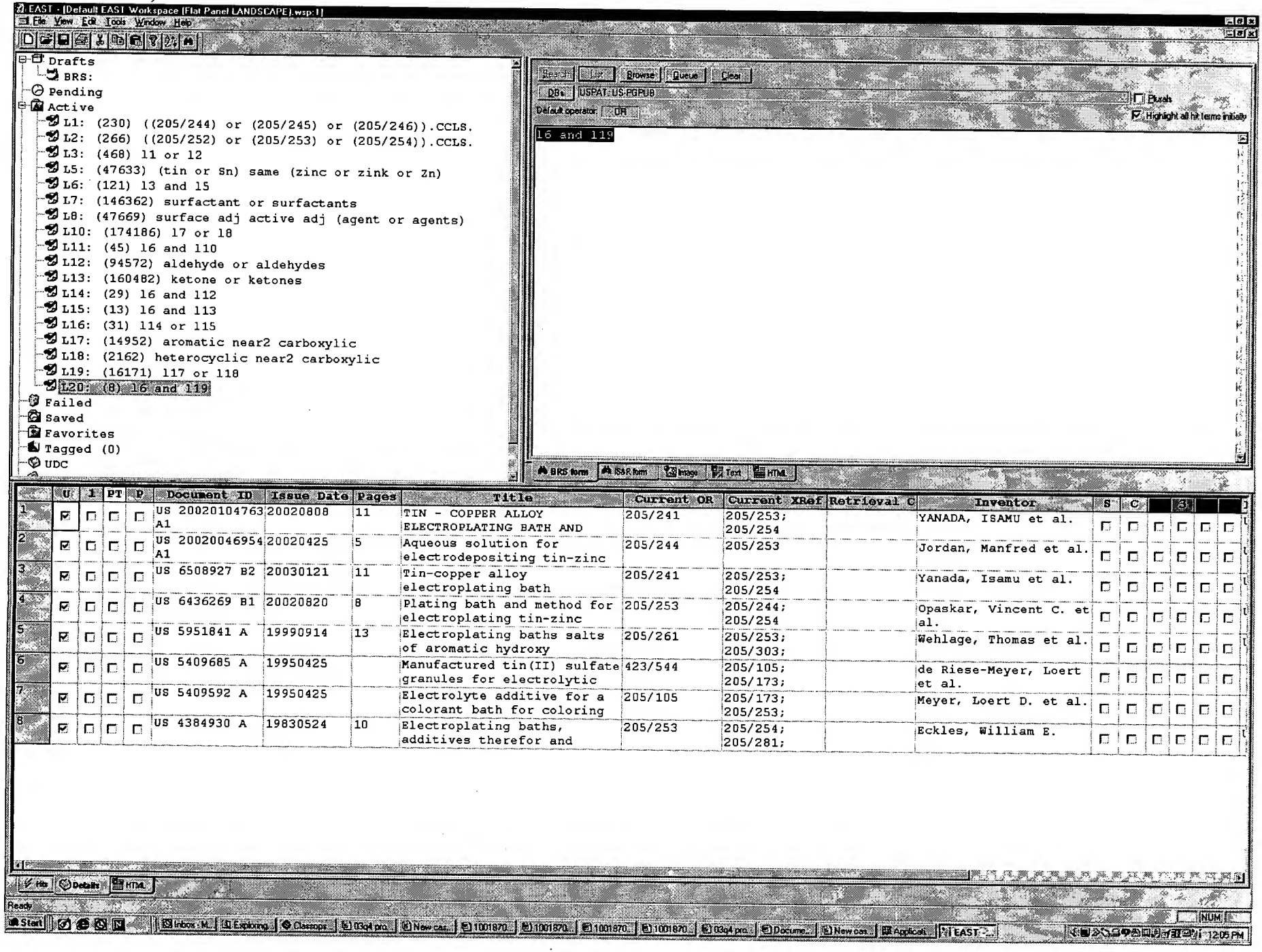
1469547	4/1977	United Kingdom	204/435

Primary Examiner—G. L. Kaplan
Attorney, Agent, or Firm—Birch, Stewart, Kolasch, and Birch

[57] **ABSTRACT**

An electroplating bath for depositing tin or a tin alloy with satisfactory brightness, which comprises a mother bath of a pH-value ranging from 4 to 8 and containing citric acid or its salt, an ammonium salt and a water-soluble polymer as a brightener. The bath may further comprise an aldehyde compound as a co-brightener.

8 Claims, No Drawings



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1	☑	☐	☐	☐	US 20020104763 A1	20020808	11	TIN - COPPER ALLOY ELECTROPLATING BATH AND	205/241	205/253; 205/254		YANADA, ISAMU et al.	☐	☐	☐	☐	☐	☐
2	☑	☐	☐	☐	US 20020046954 A1	20020425	5	Aqueous solution for electrodepositing tin-zinc	205/244	205/253		Jordan, Manfred et al.	☐	☐	☐	☐	☐	☐
3	☑	☐	☐	☐	US 6508927 B2	20030121	11	Tin-copper alloy electroplating bath	205/241	205/253; 205/254		Yanada, Isamu et al.	☐	☐	☐	☐	☐	☐
4	☑	☐	☐	☐	US 6436269 B1	20020820	8	Plating bath and method for electroplating tin-zinc	205/253	205/244; 205/254		Opaskar, Vincent C. et al.	☐	☐	☐	☐	☐	☐
5	☑	☐	☐	☐	US 5951841 A	19990914	13	Electroplating baths salts of aromatic hydroxy	205/261	205/253; 205/303;		Wehlage, Thomas et al.	☐	☐	☐	☐	☐	☐
6	☑	☐	☐	☐	US 5409685 A	19950425		Manufactured tin(II) sulfate granules for electrolytic	423/544	205/105; 205/173;		de Riese-Meyer, Loert et al.	☐	☐	☐	☐	☐	☐
7	☑	☐	☐	☐	US 5409592 A	19950425		Electrolyte additive for a colorant bath for coloring	205/105	205/173; 205/253;		Meyer, Loert D. et al.	☐	☐	☐	☐	☐	☐
8	☑	☐	☐	☐	US 4384930 A	19830524	10	Electroplating baths, additives therefor and	205/253	205/254; 205/281;		Eckles, William E.	☐	☐	☐	☐	☐	☐

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US-PAT-NO: 5951841

DOCUMENT-IDENTIFIER: US 5951841 A
See image for Certificate of Correction

TITLE: Electroplating baths salts of aromatic hydroxy compounds and their use as brighteners

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Brief Summary Text - BSTX (4):
In the electrodeposition of metals or alloys, in particular of zinc or tin or zinc alloys or tin alloys, onto metallic substrates, such as shaped metal articles or metallated plastic shaped articles, from aqueous acidic solution, a bright coating is frequently desirable in order to give the electroplated article an advantageous decorative appearance. Thus, in addition to the corrosion-inhibiting effect or an effect which improves the mechanical properties of the shaped article, a decorative effect is often desirable. In order to obtain the desired effects, it is essential that the electroplating baths contain certain assistants, since otherwise the metal coatings being deposited from acidic solution are generally dull and frequently also irregular. A group of such assistants for acidic electroplating baths comprises, for example, conductive salts which are used for improving the conductivity of the baths. Another group of assists comprises the brighteners.

Brief Summary Text - BSTX (5):
U.S. Pat. No. 3,694,330 (Reissue 27 999) discloses acidic electroplating zinc baths which contain ammonium salts and, as brighteners, aromatic carbonyl compounds. Aromatic carboxylic acids and aromatic aldehydes and ketones are mentioned as the latter. Explicitly mentioned are, inter alia, cinnamic acid, cinnamaldehyde, benzoic acid, benzalacetone and ethyl benzoylacetate.

Brief Summary Text - BSTX (177):
Preferred metal salts are zinc salts and tin salts.

Brief Summary Text - BSTX (181):
The novel aqueous acidic electroplating baths have the usual compositions with regard to the other components. They contain, for example, 50-150 g/l of zinc chloride or the equivalent amount of zinc sulfate. If alloys of zinc, for example with cobalt and/or nickel and/or iron, are to be deposited onto metallic shaped articles, the baths additionally contain, as a rule, 1-30 g/l of cobalt sulfate and/or nickel sulfate and/or iron sulfate or the equivalent amount of another, water-soluble cobalt and/or nickel and/or iron salt. It is also possible to use the corresponding tin salts in equivalent amounts.

Claims Text - CLTX (144):
9. An acidic electroplating bath as claimed in claim 1, wherein the bath comprises at least one metal salt selected from the group consisting of zinc salts and tin salts.

United States Patent [19]

Wehlage et al.

[11] **Patent Number: 5,951,841**

[45] **Date of Patent: Sep. 14, 1999**

[54] **ELECTROPLATING BATHS SALTS OF AROMATIC HYDROXY COMPOUNDS AND THEIR USE AS BRIGHTENERS**

[75] Inventors: **Thomas Wehlage**, Speyer; **Ulrich Schröder**, Frankenthal; **Alfred Oftring**, Bad Dürkheim, all of Germany

[73] Assignee: **BASF Aktiengesellschaft**, Ludcigshafen, Germany

[21] Appl. No.: **08/860,301**

[22] PCT Filed: **Dec. 22, 1995**

[86] PCT No.: **PCT/EP95/05090**

§ 371 Date: **Oct. 6, 1997**

§ 102(e) Date: **Oct. 6, 1997**

[87] PCT Pub. No.: **WO96/20152**

PCT Pub. Date: **Jul. 4, 1996**

[30] **Foreign Application Priority Data**

Dec. 23, 1994 [DE] Germany 44 46 329

[51] **Int. Cl.**[6] **C25D 3/00**

[52] **U.S. Cl.** **205/261**; 205/253; 205/303; 205/314; 549/287; 558/401; 560/51; 564/123; 568/308

[58] **Field of Search** 205/253, 302, 205/303, 307, 308, 311, 312, 314, 261; 106/1.05; 549/287; 558/401; 568/308; 560/51; 564/123

[56] **References Cited**

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Primary Examiner—Kathryn Gorgos
Assistant Examiner—Wesley A. Nicolas
Attorney, Agent, or Firm—Oblon, Spivak, McClelland, Maier & Neustadt, P.C.

[57] **ABSTRACT**

Salts of aromatic hydroxy compounds are used as brighteners in acidic electroplating baths. Furthermore, acidic electroplating baths for the electrolytic deposition of metallic layers onto shaped articles comprise, as brighteners, at least one novel salt of an aromatic hydroxy compound. Finally, shaped articles are electroplated by a process using the novel acidic electroplating baths.

17 Claims, No Drawings

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6	US 4384930 A	10								USPAT
7	US 20020104763 A	11								US-PG

US-PAT-NO: 5409592

DOCUMENT-IDENTIFIER: US 5409592 A

TITLE: Electrolyte additive for a colorant bath for coloring aluminum and process for coloring aluminum

---------- KWIC ---------

Brief Summary Text - BSTX (18):

DE-A-24 28 635 describes the use of a combination of tin(II) salts and zinc salts with addition of sulfuric acid and boric acid and also aromatic carboxylic and sulfonic acids (sulfophthalic acid or sulfosalicylic acid) in the electrolytic coloring of anodically oxidized aluminum articles in grey tones. Excellent throwing of the coloring effect is said to be obtained in particular when the pH value is between 1 and 1.5. pH adjustment to 1-1.5 is a basic prerequisite for good electrolytic coloring. There is no mention of whether the organic acids added have an effect on throwing power, nor is the throwing power achieved quantitatively described.

Brief Summary Text - BSTX (28):

b) as throwing power improver at least one aromatic carboxylic acid corresponding to general formula V: ##STR2## in which R.sup.1 to R.sup.5 represent hydrogen, hydroxyl, carboxyl and/or sulfonic acid groups.

Brief Summary Text - BSTX (43):

In another embodiment, the process according to the invention is characterized in that the electrolyte contains other heavy metal salts besides tin, for example nickel, cobalt, copper and/or zinc (see Wernick, et al., loc. cit.).

Current US Cross Reference Classification - CCXR (2):

205/253

trical and geometric parameters, such as for example the shape of the workpiece or its positioning and size.

DE-A-26 09 146 describes a process for coloring in tin electrolytes, in which throwing power is established through the particular circuit and voltage arrangement.

DE-A-24 28 635 describes the use of a combination of tin(II) salts and zinc salts with addition of sulfuric acid and boric acid and also aromatic carboxylic and sulfonic acids (sulfophthalic acid or sulfosalicylic acid) in the electrolytic coloring of anodically oxidized aluminum articles in grey tones. Excellent throwing of the coloring effect is said to be obtained in particular when the pH value is between 1 and 1.5. pH adjustment to 1-1.5 is a basic prerequisite for good electrolytic coloring. There is no mention of whether the organic acids added have an effect on throwing power, nor is the throwing power achieved quantitatively described.

DE-C-32 46 704 describes a process for electrolytic coloring in which good throwing power is guaranteed by the use of special geometry in the coloring bath. In addition, cresol and phenol sulfonic acid, organic substances, such as dextrin and/or thiourea and/or gelatine, are said to guarantee uniform coloring. The disadvantage of this process lies in the high capital outlay involved in installation of the necessary equipment. The addition of deposition inhibitors, such as dextrin, thiourea and gelatin, has only a slight influence on throwing power because the deposition process in electrolytic coloring differs significantly from that in electro-tin-plating. There is also no reference in the document in question to possible methods of measuring the improvements in throwing power.

In addition, European patent application EP-A-354 365 describes a process for the electrolytic coloring of anodized aluminum surfaces using metal salts, in which the antioxidants corresponding to general formulae I and IV (cf. the claims) are used together with the throwing power improvers p-toluene sulfonic acid and/or naphthalene sulfonic acid. However, the throwing power improvers mentioned in this document lead during electrolysis to foul-smelling decomposition products so that these throwing power improvers are no longer being used.

DESCRIPTION OF THE INVENTION

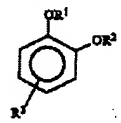
Object of the Invention

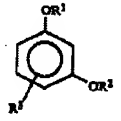
Now, the problem addressed by the present invention was to provide a new electrolyte additive for a sulfuric acid coloring bath containing tin(II) for the alternating-current coloring of anodized aluminum surfaces which would overcome the problems known from the prior art discussed in the foregoing, such as guaranteeing lasting stability of the coloring bath, avoiding the oxidation of Sn(II) and, at the same time, guaranteeing good throwing power.

SUMMARY OF THE INVENTION

Accordingly, the present invention relates to an electrolyte additive for a sulfuric acid coloring bath containing tin(II) for the alternating-current coloring of anodized aluminum surfaces containing at least one antioxidant and at least one throwing power improver, characterized in that the electrolyte additive contains

a) as antioxidant at least one compound corresponding to general formulae I to IV:


(I)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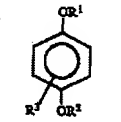
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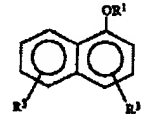
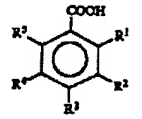

(IV)

in which

R^1 and R^2 represent hydrogen, alkyl, aryl, alkylaryl, alkylaryl sulfonic acid, alkyl sulfonic acid containing 1 to 22 carbon atoms and alkali metal salts thereof and

R^3 represents one or more hydrogen and/or alkyl, aryl, alkylaryl moieties containing 1 to 22 carbon atoms, at least one of the substituents R^1, R^2 and R^3 not being hydrogen, and

b) as throwing power improver at least one aromatic carboxylic acid corresponding to general formula V:


(V)

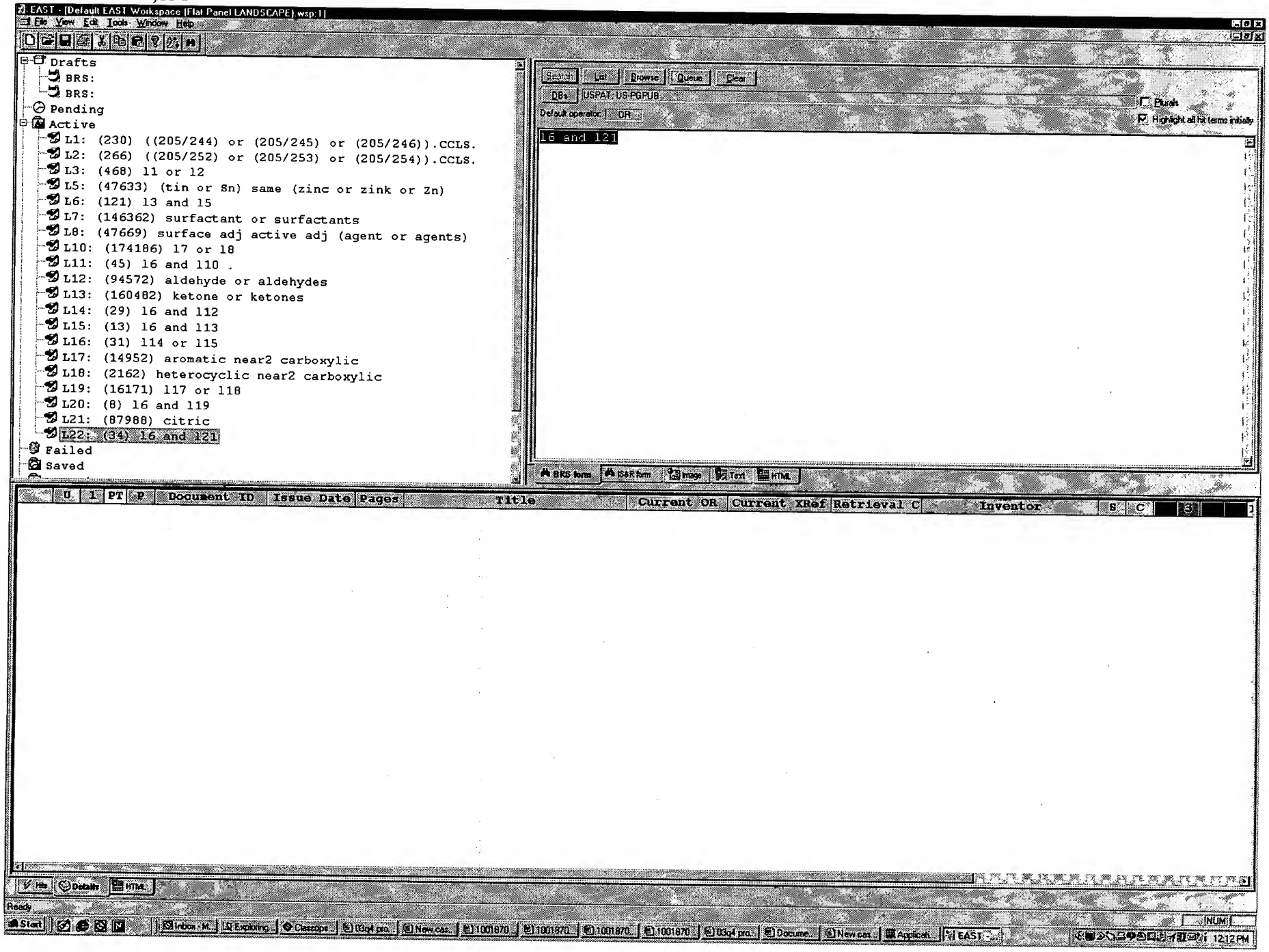
in which

R^1 to R^5 represent hydrogen, hydroxyl, carboxyl and/or sulfonic acid groups.

The present invention also relates to a process for the alternating-current coloring of anodized aluminum surfaces in a sulfuric acid coloring bath containing tin(II), characterized in that an electrolyte additive as defined above is used for electrolytic coloring in the sulfuric acid coloring bath containing tin(II) at a pH value of 0.1 to 2.0, at a temperature of 10° to 30 ° C. and with an alternating current voltage with a frequency of 50 to 60 hertz and a terminal voltage of 10 to 25 V.

A major advantage of the electrolyte additive according to the invention lies in the use of oxidation-stable, water-soluble throwing power improvers. It is particularly after relatively long periods of operation that

(claims 1, 2, 3)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L1: (230) ((205/244) or (205/245) or (205/246)).CCLS.
L2: (266) ((205/252) or (205/253) or (205/254)).CCLS.
L3: (468) l1 or l2
L5: (47633) (tin or Sn) same (zinc or zink or Zn)
L6: (121) l3 and l5
L7: (146362) surfactant or surfactants
L8: (47669) surface adj active adj (agent or agents)
L10: (174186) l7 or l8
L11: (45) l6 and l10
L12: (94572) aldehyde or aldehydes
L13: (160482) ketone or ketones
L14: (29) l6 and l12
L15: (13) l6 and l13
L16: (31) l14 or l15
L17: (14952) aromatic near2 carboxylic
L18: (2162) heterocyclic near2 carboxylic
L19: (16171) l17 or l18
L20: (8) l6 and l19
L21: (87988) citric
L22: (34) l6 and l21
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4	US 6436269 B1	8				☑				USPAT
5	US 6183545 B1	7				☑				USPAT
6	US 6176996 B1	4				☑				USPAT
7	US 5618402 A	5			☑					USPAT

US-PAT-NO: 6176996

DOCUMENT-IDENTIFIER: US 6176996 B1

TITLE: Tin alloy plating compositions

---------- KWIC ---------

Abstract Text - ABTX (1):
A tin-based, two-component alloy electroplating composition comprising 20 to 500 g/l of a tin salt, 1 to 100 g/l of a metal salt selected from the group consisting of a zinc, cobalt, bismuth and copper salt, 20 to 200 g/l of methanesulfonic acid, 10 to 300 g/l of a conductive compound, and 0.5 to 50 g/l of a complexing agent provides a plating layer having excellent corrosion resistance and solderability to electronic devices such as lead frames, connectors and printed circuit boards.

Brief Summary Text - BSTX (11):
In accordance with one aspect of the present invention, there is provided a tin alloy electroplating composition comprising 20 to 500 g/l of a tin salt, 1 to 100 g/l of a metal salt selected from the group consisting of a zinc, cobalt, bismuth and copper salt, 20 to 200 g/l of methanesulfonic acid, 10 to 300 g/l of a conductive compound, and 0.5 to 50 g/l of a completing agent.

Brief Summary Text - BSTX (13):
The novel tin alloy plating composition of the present invention comprises: two metallic components, i.e., tin and a second metal selected from the group consisting of zinc, cobalt, bismuth and copper; methanesulfonic acid; a conductive compound and a complexing agent. As a source of tin, various tin compounds such as stannous methanesulfonate, stannous sulfate, stannous chloride and sodium stannate are employed in an amount ranging from 20 to 500 g/l in the composition.

Brief Summary Text - BSTX (17):
The conductive compound used in the inventive plating composition not only further enhances the conductivity of metal ions but also increases the stability of the plating composition to provide uniform plating and an improved current efficiency. The conductive compound may include various acids and salts thereof. Preferable conductive compounds are citric acid, sulfuric acid, ammonium sulfate, ammonium citrate, sodium acetate, sodium carbonate, sodium gluconate or potassium pyrophosphate. One or more conductive compounds may be employed in an amount ranging from 10 to 300 g/l in the inventive composition.

Detailed Description Text - DETX (13):
1 L of a tin-zinc alloy plating composition was prepared by dissolving the following ingredients in distilled water.

Detailed Description Text - DETX (14):
A lead frame was plated with 1 L of the resulting tin-zinc alloy plating composition at an electric current of 10 A/dm.sup.2 to give an alloy plating

(12) **United States Patent**
Moon

(10) **Patent No.: US 6,176,996 B1**
(45) **Date of Patent: Jan. 23, 2001**

(54) **TIN ALLOY PLATING COMPOSITIONS**

(76) Inventor: **Sungsoo Moon**, #265-12, Hakjang-dong, Sasang-gu, Pusan (KR), 617-020

(*) Notice: Under 35 U.S.C. 154(b), the term of this patent shall be extended for 0 days.

(21) Appl. No.: **09/181,395**

(22) Filed: **Oct. 28, 1998**

(30) **Foreign Application Priority Data**

Oct. 30, 1997 (KR) 97-56368

(51) **Int. Cl.**[7] **C25D 3/56**
(52) **U.S. Cl.** **205/254**; 205/253; 106/1.25
(58) **Field of Search** 205/254–252; 106/1.25

(56) **References Cited**

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Primary Examiner—Kishor Mayekar
(74) *Attorney, Agent, or Firm*—Anderson Kill & Olick, PC

(57) **ABSTRACT**

A tin-based, two-component alloy electroplating composition comprising 20 to 500 g/l of a tin salt, 1 to 100 g/l of a metal salt selected from the group consisting of a zinc, cobalt, bismuth and copper salt, 20 to 200 g/l of methanesulfonic acid, 10 to 300 g/l of a conductive compound, and 0.5 to 50 g/l of a complexing agent provides a plating layer having excellent corrosion resistance and solderability to electronic devices such as lead frames, connectors and printed circuit boards.

7 Claims, No Drawings

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5	US 6183545 B1	7				S				USPAT
6	US 6176996 B1	4				S				USPAT
7	US 5618402 A	5				S				USPAT

alloy electroplating bath is not particularly limited in the present invention, it is preferably 0.01 to 30 g/l, more preferably 0.3 to 15 g/l. When it is below 0.01 g/l, the effect is insufficient and, on the contrary, when it exceeds 30 g/l, the bath is foamed during the plating and the current efficiency is lowered.

Detailed Description Text - DETX (12):

The tin-zinc alloy electroplating baths of the present invention include, for example, an alkaline cyanide bath, pyrophosphate bath, borofluoride bath, silicofluoride bath, sulfonate bath, carboxylate bath, cyanide-free alkaline bath, gluconate bath and organic acid bath. The bath contains a water soluble stannous salt such as stannous sulfate in an amount of usually 1 to 100 g/l (in terms of metallic tin), preferably 5 to 50 g/l, and a water soluble zinc salt such as zinc sulfate in an amount of usually 0.2 to 80 g/l (in terms of metallic zinc), preferably 25 to 40 g/l. Particularly preferred is the cyanide-free bath. The bath can contain 40 to 400 g/l of a carboxylic acid having 1 to 15 carbon atoms, preferably 3 to 7 carbon atoms such as citric acid or gluconic acid, 30 to 300 g/l of pyrophosphoric acid or 20 to 400 g/l of sulfamic acid. The pH of the bath ranges from 3 to 10.

Detailed Description Text - DETX (14):

When the plating bath of the present invention is used, an intended tin-zinc alloy coating having a thickness of, for example, 0.5 .mu.m to 0.5 mm can be formed by the electroplating on a metal such as iron, nickel, copper or an alloy of them. Further, by varying the ratio of tin to zinc in the plating bath, various tin-zinc alloy coating compositions can be obtained. For example, a composition having a zinc content of 5 to 5% by weight is used for the electric contact or the like; a composition having a zinc content of 15 to 45% by weight is used when a high resistance to an aqueous salt solution and to corrosion is necessitated; and a composition having a zinc content of 45 to 90% by weight is used for the formation of a coating having a high corrosion resistance which is to be exposed to air.

Detailed Description Text - DETX (15):

Although the electroplating conditions are not particularly limited, the plating bath temperature is preferably 10.degree. to 70.degree. C., more preferably 10.degree. to 40.degree. C. and the current density is preferably 0.1 to 10 A/dm.sup.2. The time period for the electroplating is not limited, but preferably 1 minutes to 2 hours, more preferably 5 minutes to 1 hour. In this connection, the substrate is a cathode and tin-zinc alloy is an anode. A weight ratio of tin to zinc in the anode is optional but preferably the ratio may be the same as in the alloy composition formed on the substrate.

Detailed Description Text - DETX (17):

When the tin-zinc alloy plating bath of the present invention is used, the formed coating film comprises a uniform alloy composition even in case the current density varies over a wide range. Therefore, the coating film having the uniform alloy composition can be formed even on the substrate having a complicated shape, and the chromate treatment becomes satisfactory. As a result, the effect of the coating film is improved, the resultant product is stable and the productivity is improved. Thus the tin-zinc alloy coating film having a high quality can be provided.

United States Patent [19]

Sakurai et al.

[11] **Patent Number: 5,618,402**

[45] **Date of Patent: Apr. 8, 1997**

[54] TIN-ZINC ALLOY ELECTROPLATING BATH AND METHOD FOR ELECTROPLATING USING THE SAME

[75] Inventors: **Hitoshi Sakurai**, Matsudo; **Tadahiro Ohmura**, Funabashi, both of Japan

[73] Assignee: **Dipsol Chemicals Co., Ltd.**, Tokyo, Japan

[21] Appl. No.: **180,345**

[22] Filed: **Jan. 12, 1994**

[51] **Int. Cl.**[6] **C25D 3/56**; C25D 3/60

[52] **U.S. Cl.** **205/244**; 205/252; 205/253; 205/254

[58] **Field of Search** 205/244, 252, 205/253, 254; 106/1.05, 1.25, 1.29

[56] **References Cited**

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Surface Treatment Technology Abstracts, vol. 29, No. 2, pp. 84, Mar./Apr. 1987, L. K. Bobrovskii, et al., "Electrolyte for Electrodeposition of Tin–Zinc Alloy Coatings" (nat trans Dec. 2).

Galvanotechnik, vol. 82, No. 9, p. 3046, Sep. 1991, "Galvanische Zinn–Zink–Uberzuge Als Cadmiumersatz" (nat trans Dec. 2).

Primary Examiner—Kathryn L. Gorgos
Assistant Examiner—Edna Wong
Attorney, Agent, or Firm—Oblon, Spivak, McClelland, Maier & Neustadt, P.C.

[57] **ABSTRACT**

A tin-zinc alloy electroplating bath comprises an amphoteric surfactant, a water-soluble stannous salt, a water-soluble zinc salt and a balance of water. When the tin-zinc alloy plating bath of the present invention is used, the formed coating film comprises a uniform alloy composition even in case where the current density varies over a wide range. Therefore, the coating film having the uniform alloy composition can be formed even on the substrate having a complicated shape and the chromate treatment becomes satisfactory. As a result, the effect of the coating is improved, the resultant product is stable and the productivity is improved. Thus the tin-zinc alloy coating film having a high quality can be provided.

16 Claims, No Drawings

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9	US 5514261 A	6				☑				USPAT
10	US 5409685 A	7				☑				USPAT
11	US 5409592 A	6				☑				USPAT
12	US 4904544 A	7				☑				USPAT
13	US 4801368 A	10				☑				USPAT
14	US 4717458 A	10				☑				USPAT

Brief Summary Text - BSTX (46):

Zinc alloy baths may also contain various other additives or agents. In some cases a particular additive or agent may be useful for more than one purpose. Examples of additional ingredients which may be employed in the zinc alloy baths include buffers and bath modifiers such as boric acid, acetic acid, ammonium sulfate, sodium acetate, ammonium chloride and the like. For chloride containing baths, carriers such as polyalkoxylated ethers such as alcohols, phenols, napthols or acetylenic glycols and their anionic and cationic derivatives may be added. Aromatic carbonyl compounds such as benzylidene acetone, chlorobenzaldehyde, cinnamic acid, benzoic acid, or nicotinic acid may also be used to enhance leveling and brightness. Additionally, to further enhance brightness, sulfonimides and sulfonimides can be employed in chloride and/or sulfate containing baths of the types described in copending U.S. patent application Ser. No. 850,465, filed Apr. 15, 1986, the teachings of which are incorporated herein by reference. Zinc alloy baths may also contain conductive salts, such as ammonium sulfate, ammonium chloride, sodium and/or potassium chloride, ammonium fluoroborate, magnesium sulfate, sodium sulfate, and the like, to improve the conductivity of the bath. Additional supportive additives such as aluminum sulfate, polyacrylamides, thioureas, or the like may also be added to the bath to improve the crystal structure of the zinc alloy plate obtained and provide the desired appearance to the alloy deposit. Neutral baths may contain common chelating agents to keep the metal ions in solution. The preferred chelating agents are citric acid, gluconic acid, glucoheptanoic acid, tartaric acid as well as their alkali metal, ammonium, zinc, cobalt, or nickel salts. Also triethanolamine may be used. The quantities used should be enough to keep the metals in solution at pH 6-8.9.

Brief Summary Text - BSTX (50):

To further enhance the corrosion resistance of the alloy deposit, small amounts of trace metals which will codeposit with the zinc alloy may be added to the electroyte. For example, soluble salts of chromium, titanium, tin, cadmium, or indium may be added to the bath in amounts of 5 mg/l to 4 g/l.

Brief Summary Text - BSTX (61):

The zinc-iron alloy electroplating bath can range in pH from about 0 up to about 6.5, preferably from about 0.5 to about 5. When the bath is weakly acidic or near neutral, such as at a pH of about 3 to about 6.5, it is preferred to incorporate conventional complexing or chelating agents to maintain an effective amount of the metal ions in solution. The preferred chelating or complexing agents are citric acid, gluconic acid, glucoheptanoic acid, tartaric acid, ascorbic acid, isoascorbic acid, malic acid, glutaric acid, muconic acid, glutamic acid, glycollic acid, aspartic acid, and the like as well as their alkali metal, ammonium, zinc or ferrous salts thereof. Additionally, suitable complexing or chelating agents that can be employed include nitrilo triacetic acid, ethylene diamine tetraethanol and ethylene diamine tetra acetic acid and salts thereof.

Current US Original Classification - CCOR (1):

205/246

Current US Cross Reference Classification - CCXR (1):

205/245

United States Patent [19]

Martin et al.

[11] **Patent Number: 4,717,458**

[45] **Date of Patent: Jan. 5, 1988**

[54] **ZINC AND ZINC ALLOY ELECTROLYTE AND PROCESS**

[75] **Inventors:** Sylvia Martin, Utica; Roy W. Herr, Troy; Walter J. Wiecmerniak, Utica; Alice M. Strum, Warren, all of Mich.

[73] **Assignee:** OMI International Corporation, Warren, Mich.

[21] **Appl. No.:** 920,636

[22] **Filed:** Oct. 20, 1986

[51] **Int. Cl.**[4] C25D 3/22; C25D 3/56

[52] **U.S. Cl.** 204/44.2; 204/44.5; 204/55.1

[58] **Field of Search** ..... 204/55 R, 55 Y, 44.2, 204/44.5, 114, 123

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,454,475	7/1969	Rushmere et al.	204/55 Y
4,397,718	8/1983	Martin	204/55 Y
4,401,326	8/1983	Martin	204/44.2
4,444,629	4/1984	Martin	204/44.2
4,488,942	12/1984	Martin et al.	204/44.2

Primary Examiner—G. L. Kaplan

Attorney, Agent, or Firm—Richard P. Mueller

[57] **ABSTRACT**

An aqueous bath suitable for electrodepositing zinc and alloys of zinc including zinc-nickel, zinc-cobalt, zinc-nickel-cobalt, zinc-iron, zinc-iron-nickel, zinc-iron-cobalt, and zinc-nickel-cobalt-iron containing a brightening amount of an AABB-type polyamide brightener in an amount effective to produce an electrodeposit of the desired brightness. The invention further contemplates the process of electrodepositing zinc and zinc alloys of the foregoing types on a conductive substrate employing the aqueous electrolyte.

28 Claims, No Drawings

EAST Browser - L22: [34] 6 and 21 | US 4299671 A | Tag: S | Doc: 21/34 (SORTED) | Format : KWIC

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15	US 4541903 A	8				☑				USPAT
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18	US 4486942 A	10				☑				USPAT
19	US 4428803 A	6				☑				USPAT
20	US 4401526 A	9				☑				USPAT
21	US 4299671 A	7				☑				USPAT

Brief Summary Text - BSTX (2):

The difficulties associated with the consistent electrodeposition of bright, conventional chromium deposits coupled with the imposition of government restrictions on the discharge of toxic effluents including hexavalent chromium present in conventional chromium electroplating baths has prompted the development of alternative electroplating bath compositions and techiques for depositing metal alloys intended to duplicate the color and characteristics of conventional chromium deposits. In U.S. Pat. No. 3,881,919, for exaple, an electroplating bath is disclosed for depositing a ternary alloy consisting of cobalt, tin and zinc which simulates a chromium deposit. In U.S. Pat. No. 4,035,249 which is assigned to the same assignee as the present invention, an electroplating bath composition is disclosed for depositing a binary alloy consisting of cobalt and tin. The bath composition and process as disclosed in the last mentioned U.S. patent is primarily adapted for the bulk plating of small workpieces such as in barrels and some difficulty has been encountered in adapting the bath for rack plating of workpieces.

Brief Summary Text - BSTX (7):

The complexing agent preferably comprises citric acid including the alkali metal, ammonium, zinc and cobalt salts thereof. Gluconic acid, alpha glucoheptonic acid, tartaric acid, as well as the alkali metal, ammonium, zinc, and cobalt salts thereof, can also be employed preferably in combination with at least 10% of the citric acid complexing compound.

Brief Summary Text - BSTX (15):

In addition to the cobalt and zinc ions, the electrolyte contains a controlled amount of an organic complexing agent present to maintain substantially all of the cobalt and zinc ions in solution. Complexing agents which have been found suitable in accordance with the practice of the present invention include citric acid, gluconic acid, alpha glucoheptonic acid, tartaric acid, as well as the alkali metal, ammonium, zinc, cobalt salts thereof. Of the foregoing, citric acid or the citric acid salts constitutes the preferred material. The use of citric acid and/or a citrate salt constitutes the preferred practice for electrodepositing a cobalt-zinc alloy employing rack plating techniques. On the other hand, sodium glucoheptonate appears to provide the best results when the bath is employed for bulk plating of workpieces in an electroplating barrel. The use of the alternative complexing agents and/or the salts thereof for rack plating have been found suitable for electrodepositing a cobalt-zinc alloy at a plating thickness less than about 0.1 mil. However, when electroplating the cobalt-zinc alloy in amounts greater than 0.1 mil, such alternative complexing agents have been noted to produce dark and spongy deposits in some instances, necessitating the addition of citric acid or a citrate salt in combination with the alternative complexing agent to overcome this problem. Generally, the use of the citrate complexing agent in an amount of at least about 10% of the total complexing agent present in the bath or, in amounts of at least about 5 to 10 g/l in the electrolyte provides satisfactory electrodeposits of a relatively high thickness. For the rack plating of conductive substrates employing the most preferred conditions as hereinabove described, citric acid itself present in an amount of about 40 g/l has been found most desirable.

Brief Summary Text - BSTX (16):

The concentration of the complexing agent in the electrolyte may range from

United States Patent [19]

Tremmel et al.

[11] 4,299,671

[45] Nov. 10, 1981

[54] **BATH COMPOSITION AND METHOD FOR ELECTRODEPOSITING COBALT-ZINC ALLOYS SIMULATING A CHROMIUM PLATING**

[75] Inventors: Robert A. Tremmel, Woodhaven; Walter J. Wieczerniak, Utica, both of Mich.

[73] Assignee: Hooker Chemicals & Plastics Corp., Warren, Mich.

[21] Appl. No.: 159,402

[22] Filed: Jun. 13, 1980

[51] Int. Cl.³ C25D 3/56; C25D 5/48

[52] U.S. Cl. ..... 204/35 R; 204/38 R; 204/43 Z

[58] Field of Search ..... 204/43 Z, 43 T, 123, 204/35 R, 38 R

[56] References Cited

U.S. PATENT DOCUMENTS

3,881,919 5/1975 Hyner et al. ..... 204/43 S X

4,035,249 7/1977 Wieczerniak ..... 204/43 S

FOREIGN PATENT DOCUMENTS

234296 10/1969 U.S.S.R. ..... 204/43 Z

Primary Examiner—G. L. Kaplan

Attorney, Agent, or Firm—Richard P. Mueller

[57] **ABSTRACT**

A bath composition and method for electrodepositing a cobalt-zinc alloy on a conductive substrate which simulates the appearance of a conventional chromium electrodeposit. The bath comprises an aqueous solution having a pH of about 6 to about 9 containing a controlled ratio of cobalt ions and zinc ions and a complexing agent sufficient to maintain the cobalt and zinc ions in solution. The bath and method are particularly adaptable for rack plating articles to impart a decorative bright chromium-like appearance and semi-bright deposits simulating conventional chromium platings.

40 Claims, No Drawings

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